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Greiner | Neise | Stöcker

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Walter Greiner | Ludwig Neise | Horst Stöcker

THERMODYNAMICS AND STATISTICAL MECHANICS

With 186 figures

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Foreword

More than a generation of German-speaking students around the world have worked their way to an understanding and appreciation of the power and beauty of modern theoretical physics—with mathematics, the most fundamental of sciences—using Walter Greiner's textbooks as their guide.

The idea of developing a coherent, complete presentation of an entire field of science in a series of closely related textbooks is not a new one. Many older physicians remember with real pleasure their sense of adventure and discovery as they worked their ways through the classic series by Sommerfeld, by Planck and by Landau and Lifshitz. From the students' viewpoint, there are a great many obvious advantages to be gained through use of consistent notation, logical ordering of topics and coherence of presentation; beyond this, the complete coverage of the science provides a unique opportunity for the author to convey his personal enthusiasm and love for his subject.

These volumes on classical physics, finally available in English, complement Greiner's texts on quantum physics, most of which have been available to English-speaking audiences for some time. The complete set of books will thus provide a coherent view of physics that includes, in classical physics, thermodynamics and statistical mechanics, classical dynamics, electromagnetism, and general relativity; and in quantum physics, quantum mechanics, symmetries, relativistic quantum mechanics, quantum electro- and chromodynamics, and the gauge theory of weak interactions.

What makes Greiner's volumes of particular value to the student and professor alike is their completeness. Greiner avoids the all too common "it follows that. . . " which conceals several pages of mathematical manipulation and confounds the student. He does not hesitate to include experimental data to illuminate or illustrate a theoretical point and these data, like the theoretical content, have been kept up to date and topical through frequent revision and expansion of the lecture notes upon which these volumes are based.

Moreover, Greiner greatly increases the value of his presentation by including something like one hundred completely worked examples in each volume. Nothing is of greater importance to the student than seeing, in detail, how the theoretical concepts and tools under study are applied to actual problems of interest to a working physicists. And, finally, Greiner adds brief biographical sketches to each chapter covering the people responsible

for the development of the theoretical ideas and/or the experimental data presented. It was Auguste Comte (1789–1857) in his *Positive Philosophy* who noted, "To understand a science it is necessary to know its history." This is all too often forgotten in modern physics teaching and the bridges that Greiner builds to the pioneering figures of our science upon whose work we build are welcome ones.

Greiner's lectures, which underlie these volumes, are internationally noted for their clarity, their completeness and for the effort that he has devoted to making physics an integral whole; his enthusiasm for his sciences is contagious and shines through almost every page.

These volumes represent only a part of a unique and Herculean effort to make all of theoretical physics accessible to the interested student. Beyond that, they are of enormous value to the professional physicist and to all others working with quantum phenomena. Again and again the reader will find that, after dipping into a particular volume to review a specific topic, he will end up browsing, caught up by often fascinating new insights and developments with which he had not previously been familiar.

Having used a number of Greiner's volumes in their original German in my teaching and research at Yale, I welcome these new and revised English translations and would recommend them enthusiastically to anyone searching for a coherent overview of physics.

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Preface

Thermodynamics and Statistical Mechanics contains the lectures that form part of the course in theoretical physics at the Johann Wolfgang Goethe-University in Frankfurt am Main. The lectures are given for students in physics in their fifth or sixth semester and are preceded by Theoretical Mechanics I (first semester), Theoretical Mechanics II (second semester), Classical Electrodynamics (third semester), Quantum Mechanics I (fourth semester), and Quantum Mechanics II—Symmetries and Relativistic Quantum Mechanics (fifth semester). Graduate course work, which begins with Quantum Mechanics II and Thermodynamics and Statistics, continues with Quantum Electrodynamics, the Gauge Theory of Weak Interactions, Quantum Chromodynamics, and other, more specialized courses in Nuclear and Solid State Theory, Cosmology, etc.

As in all other fields mentioned, we present thermodynamics and statistics according to the inductive method which comes closest to the methodology of the research physicist. Starting from some key experimental observations, the framework of the theory is developed and, after the basic equations are obtained, new phenomena are investigated from thereon.

The first part of the book covers basic thermodynamics with its wide range of applications in physics, chemistry and engineering. A large variety of examples and applications, as well as detailed descriptions of the necessary mathematical tools, are inserted to guide the reader through this vast field. Emphasis is laid on the microscopic understanding and interpretation of macroscopic processes. Among the subjects covered in this first part are the statistical interpretation of temperature and entropy (which is discussed in great detail, especially in the second part of this volume), thermodynamic machines, phase transitions and chemical reactions.

The second part deals with statistical mechanics. Microcanonical, canonical and macrocanonical ensembles are introduced and their various applications (ideal and real gases, fluctuations, paramagnetism and phase transitions) are demonstrated.

The third part covers quantum statistics. Beginning with ideal quantum gases, we discuss Fermi- and Bose gases and show their multiple applications which stretch from solid state physics to astrophysics (neutron stars and white dwarfs) and nuclear physics (nuclei, hadronic matter and the possible phase transition to a Quark Gluon Plasma).

The last part of this book presents a survey of real gases and phase transitions. Mayer's cluster expansion and the Ising- and Heisenberg- models serve as a basis for an introduction into this challenging new field of scientific research.

These lectures are now up for their third German edition. Over the years many students and collaborators have helped to work out exercises and illustrative examples. For this first English edition we enjoyed the enthusiastic input by Steffen A. Bass, Adrian Dumitru, Dirk Rischke (now at Columbia University) and Thomas Schönfeld. Miss Astrid Steidl drew the graphs and pictures. To all of them we express our sincere thanks. We are also grateful to Professor Jes Madsen of Aarhus University in Denmark and Professor Laszlo Csernai of the University Bergen in Norway for their valuable comments on the text and illustrations. We especially thank Professor Martin Gelfand from Colorado State University in Fort Collins and his group of students who collected numerous misprints and drew our attention to several physical problems.

Finally, we wish to thank Springer-Verlag New York, in particular Dr. Hans-Ulrich Daniel and Dr. Thomas von Foerster for their encouragement and patience, and Ms. Margaret Marynowski, for her expertise in copyediting the English edition.

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PART I

THERMODYNAMICS

1 Equilibrium and State Quantities

Introduction

The theoretical description of systems consisting of very many particles is the center of interest in this volume of the series of lessons in *Theoretical Physics*. Such many-particle systems can be found everywhere in nature: on the one hand, e.g., the atoms and molecules in gases, fluids, solids or plasmas (with most of which one has daily experience) or on the other hand, the quantum gas of electrons in semiconductors or metals.

In burnt-out suns (white dwarfs) one finds the electron gas and nuclear matter (in the center of neutron stars and in supernova explosions), which consists of many neutrons and protons. Our universe was created in the "big bang" from a many-particle system of leptons, quarks and gluons.

In the following we will see that all these completely different systems obey common and very general physical laws. In particular, we will discuss the properties of such many-particle systems in thermodynamic equilibrium. Special emphasis will be laid on the microscopic point of view of statistical mechanics. Nevertheless, classical macroscopic thermodynamics shall not fall short, since it is of great importance: the concepts of thermodynamics are very general and to a great extent independent of special physical models, so that they are applicable in many fields of physics and the technical sciences.

The task of thermodynamics is to define appropriate physical quantities (the *state quantities*), which characterize macroscopic properties of matter, the so-called *macrostate*, in a way which is as unambiguous as possible, and to relate these quantities by means of universally valid equations (the *equations of state* and the *laws of thermodynamics*). Proceeding from daily experience one first sets up relations which seem to have general validity independent of the special physical system under consideration. These relations are the axiomatic laws of thermodynamics. Hence in the beginning, we have to define certain state quantities to formulate and substantiate the laws of thermodynamics, i.e., the energy law and the entropy law. These laws are, however, supplemented by a variety of empirically established relations between the state quantities (the equations of state), which are valid only for special physical systems. It is then sufficient to specify a few state quantities, called *state variables*, so that all other state quantities have certain uniquely

defined values. Thermodynamics cannot and will not give reasons why a certain equation of state describes a system. It restricts itself to making assertions concerning the state quantities, if a particular equation of state is given. It is already of great value to know that an equation of state exists at all (even if one cannot give it in explicit form), to explain certain general relationships.

However, the generality of thermodynamics, which is due to the fact that it is based on only a few empirical theorems, causes simultaneously a major restriction. The state quantities are phenomenologically defined by means of a prescription on how to measure them. Thermodynamics cannot make any assertions concerning reasons and interpretations on the microscopic level, which for the most part depend on a physical model. In particular, the very illustrative interpretation of the central concept of heat by means of the statistical, thermal motion of particles is not a subject of thermodynamics. Nevertheless, several times we will understand certain concepts only if we anticipate ideas pertaining to the microscopic regime. As already mentioned above, we are concerned with the equilibrium state. We will therefore precisely define this fundamental term and distinguish it from stationary or nonequilibrium states. Due to this restriction, equilibrium thermodynamics is not able to describe the temporal evolution of processes. However, it is possible, by a mere comparison of equilibrium states, to decide whether a process can happen or not. Here the concept of infinitesimal changes of state is extensively used. In thermodynamics one mostly deals with functions of more than one variable; hence we will often have to handle differentials and line integrals. We will not too much bother about mathematical rigor; rather we will try to gain insight into the physical fundaments. Many students regard thermodynamics as very abstract and "dry." Hence we have included, as in the other volumes of this series, a variety of illustrative examples and problems, which shall illuminate the general notions of thermodynamics.

Systems, phases and state quantities

The concept of a thermodynamic system requires further specification. We define it to be an arbitrary amount of matter, the properties of which can be uniquely and completely described by specifying certain macroscopic parameters. The matter under consideration is confined by physical walls against the surroundings. If one makes further, special demands concerning these walls (i.e., the container), one distinguishes:

a. *Isolated systems*
These do not interact in any way with the surroundings. The container has to be impermeable to any form of energy or matter. Especially, the total energy E (mechanic, electric, etc.) is a conserved quantity for such a system and can thus be used to characterize the macrostate. The same holds for the particle number N and the volume V.

b. *Closed systems*
Here one allows only for the exchange of energy with the surroundings, but not for the exchange of matter. Thus, the energy is no longer a conserved quantity. Rather,

the actual energy of the system will fluctuate due to the energy exchange with the surroundings. However, if the closed system is in equilibrium with its surroundings, the energy will assume an average value which is related to the temperature of the system or of the surroundings. One can use the temperature, in addition to N and V, to characterize the macrostate.

c. *Open systems*
These systems can exchange energy and matter with their surroundings. Hence, neither the energy nor the particle number are conserved quantities. If the open system is in equilibrium with its surroundings, mean values of the energy and the particle number are assumed which are related to the temperature and the chemical potential (defined below). One can use the temperature and the chemical potential to characterize a macrostate.

It is obvious that at least the isolated system is an idealization, since in reality an exchange of energy with the surroundings cannot be prevented in the strict sense. However, by means of well-isolated vessels (dewars) isolated systems can be approximately realized.

If the properties of a system are the same for any part of it, one calls such a system *homogeneous*. However, if the properties change discontinuously at certain *marginal surfaces*, the system is *heterogeneous*. One calls the homogeneous parts of a heterogeneous system *phases* and the separating surfaces *phase boundaries*. A typical example for such a system is a closed pot containing water, steam and air. The phase boundary in this case is the surface of the water. One speaks of a gaseous phase (steam and air) and of a liquid phase (water). In some cases the macroscopic properties of a system depend on the size (and shape) of the phase boundaries. In our example, one has different macroscopic properties if the water covers the bottom of the pot or if it is distributed in the form of small drops (fog).

The macroscopic quantities which describe a system are called state quantities. Besides the energy E, the volume V, the particle number N, the entropy S, the temperature T, the pressure p and the chemical potential μ, such quantities include also the charge, the dipole momentum, the refractive index, the viscosity, the chemical composition and the size of phase boundaries. On the other hand, microscopic properties, e.g., the positions or momenta of the constituent particles, do not fall under the definition of state quantities. We will see later on (cf., the Gibbs phase rule) that the number of state quantities which are necessary for a unique determination of a thermodynamic state is closely related to the number of phases of a system. It is sufficient to choose a few state quantities (state variables), such that all other state quantities assume values which depend on the chosen state variables. The equations which in this way relate state quantities are called equations of state. The equations of state of a system have to be specified by empirical means. To this end one often uses polynomials of the state variables, the coefficients of which are then experimentally determined. It is important to realize that in most cases such empirical equations of state are in reasonable accordance with experiments only in a very limited range of values of the state variables. In particular, we refer in this context to the concept of the ideal gas, which one often uses as a model for real gases, but which allows for reliable assertions only in the limit of low density.

In general one distinguishes two classes of state quantities:

a. *Extensive (additive) state quantities*
These quantities are proportional to the amount of matter in a system, e.g., to the particle number or mass. Characteristic examples of extensive properties are the volume and the energy. In particular, an extensive state quantity of a heterogeneous system is *additively* composed of the corresponding extensive properties of the single phases. Thus, the volume of a pot containing water, steam and air is the sum of the volumes of the fluid and gaseous phases. The most characteristic extensive state quantity for thermodynamics (and statistical mechanics) is the entropy, which is closely related to the microscopic probability of a state.

b. *Intensive state quantities*
These quantities are independent of the amount of matter and are not additive for the particular phases of a system. They might assume different values in different phases, but this is not necessarily the case. Examples are: refractive index, density, pressure, temperature, etc. Typically, intensive state quantities can be defined locally; i.e., they may vary spatially. Consider, for instance, the density of the atmosphere, which is largest at the surface of the earth and continuously decreases with height, or the water pressure in an ocean, which increases with increasing depth.

For the moment, however, we will confine ourselves to spatially constant intensive properties. To determine the spatial dependences of intensive state variables requires additional equations (e.g., from hydrodynamics), or one has to use further equations of state (without exact knowledge about their origin). One often passes over from extensive state quantities to intensive state quantities which essentially describe very similar physical properties. For example, the energy, the volume and the particle number are extensive quantities, while the energy per unit volume (energy density) or the energy per particle, as well as the volume per particle, are intensive state quantities. Extensive variables change in proportion to the size of a system (if the intensive properties do not change and if we neglect surface effects), but this does not yield any new insight into the thermal properties of the system.

Equilibrium and temperature—the zeroth law of thermodynamics

Temperature is a state quantity which is unknown in mechanics and electrodynamics. It is specially introduced for thermodynamics, and its definition is closely connected with the concept of (thermal) equilibrium. *Equality of temperature* of two bodies is the condition for thermal equilibrium between these bodies. *Thermodynamic state quantities are defined (and measurable) only in equilibrium.*

Here the *equilibrium state* is defined as the one macroscopic state of a closed system which is automatically attained after a sufficiently long period of time such that the macroscopic state quantities no longer change with time. However, it requires some caution to use the notion of thermodynamic equilibrium for such a system. For example, it is not yet clear whether our universe is converging toward such an equilibrium state. Thus we

exclusively restrict our considerations to situations where the existence of an equilibrium state is obvious. It is often reasonable to speak of thermodynamic equilibrium even if the state quantities still change very slowly. For instance, our sun is by no means in an equilibrium state (it continuously loses energy through radiation). Nevertheless, the application of thermodynamic state quantities makes sense in this case, since the changes proceed very slowly. Suppose that, in an isolated system, one brings two partial systems, each formerly in equilibrium, into thermal contact (no exchange of matter) with each other. Then one observes, in general, various processes which are connected with a change of the state quantities, until after a sufficiently long time a new equilibrium state is attained. One calls this state thermal equilibrium. As experience has shown, all systems which are in thermal equilibrium with a given system are also in thermal equilibrium with each other. Since this empirical fact, which we will use as the foundation of our definition of temperature, is very important, one calls it also the *zeroth law of thermodynamics*.

Hence systems which are in thermal equilibrium with each other have a common intensive property, which we denote as *temperature*. Therefore, systems which are not in thermal equilibrium with each other have different temperatures. However, thermodynamics tells us nothing about the time which passes until thermal equilibrium is reached. We now can precisely define the notion of temperature by specifying how and in which units temperature is to be measured. The measurement is done as follows: a system whose thermal equilibrium state is uniquely connected with an easily observable state quantity (i.e., a thermometer), is brought into thermal equilibrium with the system whose temperature is to be measured. The state quantity to be observed can be, for instance, the volume of a fluid (fluid thermometer) or of a gas (gas thermometer), but the resistance of certain conducting materials is also suitable (resistance thermometer).

We want to mention at this point that the concept of temperature can also be extended to systems which are not as a whole in thermal equilibrium. This is possible as long as one can divide the total system into partial systems, to which one can assign local (position-dependent) temperatures. In this case, the system is not in so-called global equilibrium, but rather is in local thermal equilibrium. We encounter such systems, for example, in heavy-ion collisions or in stars, where different zones may have different temperatures.

Moreover, it is not necessarily essential to put the measuring apparatus (thermometer) in direct contact with the system (in thermal equilibrium). For instance, the surface temperature of the sun or the temperature of the flame of a burner can be determined by measuring the spectrum of the emitted electromagnetic radiation. The supposition is that the local thermal equilibrium is not essentially disturbed by the processes which happen (radiation). We will return to these questions when we discuss global and local equilibrium more extensively.

As we can see, the procedure of measuring the temperature is connected with an equation of state, i.e., the relationship between the observed state quantity (volume, resistance) and the temperature. Therefore, we also have to choose a standard system by means of which we can fix a general temperature scale. Here one exploits the fact that many different kinds of gases behave similarly if they are dilute. One can use the volume of a certain definite amount of such a gas (at a certain non vanishing pressure) as a measure for the temperature, and can calibrate other thermometers accordingly. We define the thermodynamic

temperature T with the help of the volume of such a dilute gas as

$$T = T_0 \frac{V}{V_0} \tag{1.1}$$

at constant pressure and constant particle number. See Figure 1.1.

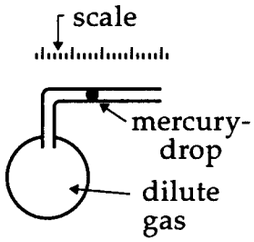

Figure 1.1. Gas thermometer.

By defining a particular temperature T_0 for a standard volume V_0 (e.g., at a pressure of one atmosphere) we can consequently also fix the scale. Today one usually takes the melting point of ice as $T = 273.15$ K, where the unit is named in honor of Lord Kelvin, who made important contributions to the field of thermodynamics. Historically, the unit of temperature was fixed by defining the temperature of the melting point of ice as 0°C and that of boiling water as 100°C (at atmospheric pressure), which is Celsius' scale. The conversion to Fahrenheit's scale is $y[°C] = (5/9)(x[°F]-32)$.

If one plots the volume of a dilute gas versus the temperature in °C, one finds a crossing point with the abscissa at the temperature −273.15°C (Figure 1.2).

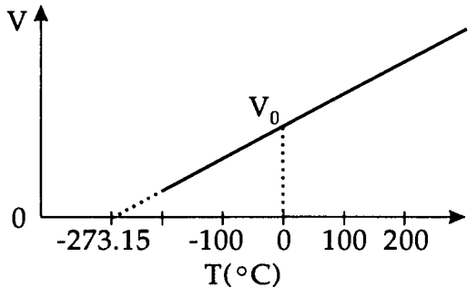

Figure 1.2. VT diagram of a dilute gas.

Of course, one cannot experimentally measure the volume of a gas at very low temperatures, since liquefaction sets in, but one can extrapolate to the crossing point. Thus we have constructed an idealized system (an ideal gas), the volume of which is just $V = 0\,\mathrm{m}^3$ at the absolute temperature (which we shall simply call the *temperature*) $T = 0$ K. At first sight, it may seem unpractical to use such an idealized system, which never can serve as a real thermometer (at low temperatures), to define the unit.

From the statistical point of view, however, we shall see that this notion of temperature yields very simple relationships in the kinetic theory of gases. For example, our absolute temperature is directly proportional to the mean kinetic energy of gas particles (cf. Example 1.1) and thus attains a simple and illustrative microscopic meaning. In particular, we can observe that there are no negative absolute temperatures in thermodynamic equilibrium, for if all particles are at rest (zero kinetic energy), the mean energy is zero and thus also the temperature. Negative kinetic energies, however, are impossible. Later on we shall see that one can nevertheless define negative temperatures for certain nonequilibrium states or subsystems.

It is of great importance to separate the notion of equilibrium from that of a stationary state. In a stationary state the macroscopic state quantities are also independent of time, but these states are always connected with an energy flux, which is not the case for equilibrium states. For instance, let us consider an electric hot plate, which can be found in many households. If one puts a pot with a meal on top of it, after some time a stationary state will be attained where the temperature of the meal will not change any longer. This, however, is not a state of thermal equilibrium as long as the surroundings have a different temperature. One must continuously supply the system with (electrical) energy to prevent the cooling of the dish, which continuously radiates energy (heat) into the surroundings. This system is not isolated, since energy is supplied as well as emitted.

Example 1.1: The ideal Gas

To illustrate the basic concepts of thermodynamics, we will consider an ideal gas in greater detail. Such an ideal gas is characterized by the fact that the particles are considered (as in classical mechanics) to be noninteracting, pointlike particles. It is obvious that this is only a simple model of a real gas, the particles of which have atomic dimensions and do interact. The approximation is the better the more dilute a gas is.

Already in 1664, R. Boyle, and shortly later (1676) but independently from him, E. Mariotte found a general relationship between the pressure and the volume of a gas at constant temperature (Figure 1.3):

$$pV = p_0V_0, \qquad T = \text{const.}$$

where we define the pressure as the force per unit area which acts perpendicularly on the area O. Microscopically, the origin of pressure is the fact that particles hit the area, where they are reflected and transfer a certain momentum. Not until 1802 did Gay-Lussac consider the dependence of the volume of a gas on temperature. The corresponding equation is identical with our definition of the absolute temperature,

$$V = \frac{T}{T_0}V_0, \qquad p = \text{const.}$$

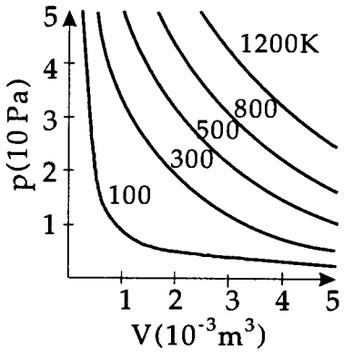

Figure 1.3. pV diagram for 1 mol of an ideal gas.

The quantities p_0, V_0, and T_0 are the pressure, volume, and temperature of an arbitrary but fixed state. Now we can ask what relationship holds between pressure, volume and temperature if we move from the state (p_0, T_0, V_0) to a final state (p, T, V). To this end we first change the pressure at constant temperature, until we reach the desired pressure p, where a volume V_0' is attained

$$pV_0' = p_0V_0, \qquad T_0 = \text{const.}$$

Now we change the temperature at constant pressure to obtain

$$V = \frac{T}{T_0}V_0', \qquad p = \text{const.}$$

If we eliminate the intermediate volume V_0' from both equations we have

$$\frac{pV}{T} = \frac{p_0V_0}{T_0} = \text{const.}$$

Since the expression pV/T is an extensive quantity it must, under the same conditions, increase proportionally to the particle number; i.e., it must equal kN, where we introduce *Boltzmann's constant of proportionality* $k = 1.380658 \cdot 10^{-23}\ \text{J K}^{-1}$. We obtain

$$\frac{pV}{T} = \frac{p_0V_0}{T_0} = Nk, \qquad pV = NkT \text{ or } p = \rho kT \tag{1.2}$$

This is the *ideal gas law,* as we will often use it; it is also an example of an equation of state: the pressure is the product of particle density ρ and the temperature.

Kinetic theory of the ideal gas

We now show that the temperature of an ideal gas can be very simply understood as the mean kinetic energy of the particles. To this end we want to introduce at this stage some concepts of statistical mechanics which will be extensively used afterwards. Each particle of the gas has a velocity vector $\vec{v}$ which will, of course, drastically change with time. For an equilibrium state, however, on average there will always be the same number of particles in a certain interval $d^3\vec{v}$ of velocity, although individual particles change their velocities. Therefore, it makes sense to ask for the probability that a particle is in the interval $d^3\vec{v}$, i.e., to speak of a *velocity distribution* in the gas which does not change with time in thermodynamic equilibrium. We do not want to consider its exact form at this point; for our purpose it is sufficient to know that such a distribution exists! (In the next example we will investigate the form of the distribution in greater detail.) We write for the number of particles $dN(\vec{v})$ in the velocity interval around $\vec{v}$

$$dN = Nf(\vec{v})\, d^3\vec{v}, \qquad f(\vec{v}) = \frac{1}{N}\frac{dN}{d^3\vec{v}} \tag{1.3}$$

where $f(\vec{v})$ is the velocity distribution, and of course it must hold that $\int_{-\infty}^{+\infty} f(\vec{v})\, d^3\vec{v} = 1$. As mentioned above, the pressure of the gas originates from the momentum transfer of the particles when they are reflected at a surface A (e.g., the wall of the box).

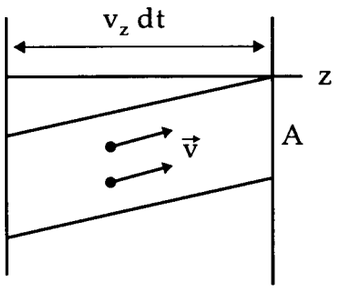

Figure 1.4. Scheme for calculating the pressure.

If we assume the z-axis of our coordinate system to be perpendicular to the area A, a particle of velocity $\vec{v}$ which hits that area transfers the momentum $p = 2mv_z$. Now the question is, how many such particles with velocity vector $\vec{v}$ hit the surface element A during a time dt? As one infers from Figure 1.4, these are just all the particles inside a parallelepiped with basis area A and height $v_z\, dt$.

All particles with velocity $\vec{v}$ travel the distance $d\vec{r} = \vec{v}\, dt$ during the time dt and therefore hit the surface, if they are somewhere inside this parallelepiped at the beginning of the time interval. On the other hand, the number of particles with velocity $\vec{v}$ inside the parallelepiped is just

$$dN = N\frac{dV}{V} f(\vec{v})\, d^3\vec{v} \tag{1.4}$$

if dV/V is the fraction of the total volume occupied by the parallelepiped. It holds that $dV = Av_z\, dt$. Each particle transfers the momentum $2mv_z$, so that the impulse per area A is

$$dF_A\, dt = 2mv_z\, dN = 2Nmv_z^2 f(\vec{v})\, d^3\vec{v}\, \frac{A\, dt}{V} \tag{1.5}$$

If we omit dt on both sides this is just the contribution of particles with velocity $\vec{v}$ to the pressure. The total pressure then results by integrating over all possible velocities with a positive component v_z (since otherwise the particles move in the opposite direction and do

not hit the wall),

$$p = \frac{1}{A}\int dF_A = \frac{N}{V}\int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y \int_0^{+\infty} dv_z f(\vec{v}) 2mv_z^2 \tag{1.6}$$

With the help of a short consideration we are now able to further evaluate the right hand side of Equation (1.6). Since the gas is at rest, the distribution $f(\vec{v})$ cannot depend on the direction of $\vec{v}$, but only on $|\vec{v}|$. Then, however, we can write the integral $\int_0^{\infty} dv_z$ as $\frac{1}{2}\int_{-\infty}^{+\infty} dv_z$ and thus obtain

$$pV = mN\int_{-\infty}^{+\infty} d^3\vec{v} f(\vec{v}) v_z^2 \tag{1.7}$$

This integral represents nothing other than the mean square of the velocity in the direction perpendicular to the surface. This mean value, however, has to be the same in all spatial directions because of the isotropy of the gas, i.e.,

$$\int d^3\vec{v} f(\vec{v}) v_z^2 \equiv \langle v_z^2\rangle = \langle v_y^2\rangle = \langle v_x^2\rangle \tag{1.8}$$

or, since $\vec{v}^2 = v_x^2 + v_y^2 + v_z^2$,

$$\langle v_z^2\rangle = \frac{1}{3}\langle \vec{v}^2\rangle = \frac{1}{3}\left(\langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle\right) \tag{1.9}$$

so that we finally have

$$pV = mN\frac{1}{3}\langle \vec{v}^2\rangle = \frac{2}{3}N\langle \epsilon_{\text{kin}}\rangle \tag{1.10}$$

Here $\langle \epsilon_{\text{kin}}\rangle = \frac{1}{2}m\langle \vec{v}^2\rangle$ is the mean kinetic energy of a particle. If we compare this with the ideal gas law, Equation (1.2), it obviously holds that $\langle \epsilon_{\text{kin}}\rangle = \frac{3}{2}kT$; i.e., the quantity kT exactly measures this mean kinetic energy of a particle in an ideal gas. In the section concerning the equipartition theorem we will see that this relationship is not restricted to an ideal gas, but can be generalized. Consequently, the importance of Boltzmann's constant k, which we introduced here only for an ideal gas, will become obvious.

Example 1.2: Maxwell's velocity distribution

We will now determine the functional form of the velocity distribution in greater detail. Because of the isotropy of the gas, $f(\vec{v})$ can be a function only of $|\vec{v}|$, or equivalently of $\vec{v}^2$. On the other hand, we may assume that the velocity distributions of the single components (v_x, v_y, and v_z) are independent of each other; i.e., it must be that

$$f\left(v_x^2 + v_y^2 + v_z^2\right) = f\left(v_x^2\right) f\left(v_y^2\right) f\left(v_z^2\right) \tag{1.11}$$

We may justify this equation in the following way: the function $f(\vec{v}^2)$ corresponds to the probability density of finding a particle with velocity $\vec{v}$. This, however, has to be proportional to the product of the probability densities of finding a particle at v_x, v_y and v_z, as long as these are statistically independent events. The only mathematical function which fulfills the

relationship (1.11) is the exponential function, so that we can write $f(\vec{v}^2) = C\exp\{a\vec{v}^2\}$, where the constants C and a must not depend on $\vec{v}$, but may be arbitrary otherwise.

If we assume the function $f(\vec{v}^2)$ to be normalizable, it must obviously hold that $a < 0$, which corresponds to a Gaussian distribution of the velocity components. The constant C can be determined from the normalization of the function $f(v_i)$ for each component,

$$1 = \int_{-\infty}^{+\infty} dv_i\, f(v_i) = C\int_{-\infty}^{+\infty} dv_i \exp\left\{-av_i^2\right\}$$

where we now have written $-a$ with $a > 0$. The value of this integral is well known; it is $\sqrt{\pi/a}$, i.e., $C = \sqrt{a/\pi}$. Now we are even able to calculate the constant a for our ideal gas, if we start from Equation (1.10)

$$\begin{aligned} kT &= m\left\langle v_z^2\right\rangle = m\int d^3\vec{v}\, f(\vec{v})v_z^2 \\ &= m\int_{-\infty}^{+\infty} dv_x f\left(v_x^2\right)\int_{-\infty}^{+\infty} dv_y f\left(v_y^2\right)\int_{-\infty}^{+\infty} dv_z v_z^2 f\left(v_z^2\right) \\ &= m\int_{-\infty}^{+\infty} dv_z f(v_z)v_z^2 \\ &= m\sqrt{\frac{a}{\pi}}\int_{-\infty}^{+\infty} dv_z \exp\left\{-av_z^2\right\} v_z^2 \\ &= 2m\sqrt{\frac{a}{\pi}}\int_0^{+\infty} dv_z \exp\{-av_z^2\}v_z^2 \end{aligned}$$

If we substitute $x = av_z^2$ we find, with $dv_z = \frac{1}{2\sqrt{a}}\frac{dx}{\sqrt{x}}$,

$$kT = 2m\sqrt{\frac{a}{\pi}}\,\frac{1}{2a\sqrt{a}}\int_0^{+\infty} dx\, e^{-x}\sqrt{x}$$

We will often encounter integrals of this type. They are solved in terms of the Γ-function, which is defined by

$$\Gamma(z) = \int_0^{+\infty} dx\, e^{-x}x^{z-1}$$

With $\Gamma(1/2) = \sqrt{\pi}$, $\Gamma(1) = 1$, and the recursion formula $\Gamma(z+1) = z\Gamma(z)$, we may readily calculate arbitrary integrals of this type for positive integer and half-integer z. We have, with $\Gamma(3/2) = 1/2\cdot\Gamma(1/2) = \sqrt{\pi}/2$,

$$kT = m\frac{1}{a\sqrt{\pi}}\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\frac{m}{a} \qquad \text{or} \quad a = \frac{m}{2kT}$$

The velocity distribution in an ideal gas for a component v_i therefore reads

$$f(v_i) = \sqrt{\frac{a}{\pi}}\exp\left\{-av_i^2\right\} = \sqrt{\frac{m}{2\pi kT}}\exp\left\{-\frac{mv_i^2}{2kT}\right\} \tag{1.12}$$

and the total distribution is

$$f(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left\{\frac{-m\vec{v}^2}{2kT}\right\} \tag{1.13}$$

These expressions are normalized and fulfill Equation (1.11). The total distribution was first derived by Maxwell and is named after him. In this derivation we have relied on several general heuristic assumptions. However, we will see that Equations (1.12) and (1.13) follow from first principles in the framework of statistical mechanics.

Pressure, work and chemical potential

In the last section we explicitly dealt with the central notion of temperature. Now we want to discuss several other state quantities. Further state quantities will be defined in the following sections. We will, in general, measure *amounts of matter* in terms of the particle number N. Since N assumes very large values for macroscopic systems, one often uses multiples of *Avogadro's number* $N_A = 6.0221367 \cdot 10^{23}$. The *atomic mass unit* u is especially convenient for measuring masses of single particles (atoms and molecules); it is defined by

$$1\,\mathrm{u} = \frac{1}{12}\,\mathrm{m}\,{}^{12}\mathrm{C} \tag{1.14}$$

i.e., via the mass of one atom of the carbon isotope ^{12}C. This unit is very useful, since atomic masses are nowadays very precisely measured in mass spectrometers which are particularly easily calibrated with carbon compounds. Avogadro's number is just the number of particles with mass 1u which altogether have the mass 1g,

$$N_A = \frac{1\,\mathrm{g}}{1\,\mathrm{u}} = 6.0221367 \cdot 10^{23} \tag{1.15}$$

The quantity N_A particles is also called 1 mole of particles. If a system consists of several kinds of particles, for instance $N_1, N_2, \ldots, N_n$ particles of n species, the so-called *molar fraction* X is a convenient quantity for measuring the chemical constitution,

$$X_i = \frac{N_i}{N_1 + N_2 + \cdots + N_n} \tag{1.16}$$

As one can see from the definition, it always holds that $\sum_i X_i = 1$. The molar fraction therefore denotes the fractional constitution of a system. It is an intensive variable and may assume different values in different phases.

The *pressure* can be understood in purely mechanical terms as a force which acts perpendicularly to a known area A.

$$p = \frac{F_\perp}{A} \tag{1.17}$$

We therefore have $[p] = \mathrm{N\,m^{-2}} = \mathrm{Pa}$ as the unit. Interestingly enough, pressure has the same dimension as energy density, since

$$1\mathrm{Nm^{-2}} = 1\mathrm{kgms^{-2}\,m^{-2}} = 1\,\mathrm{Jm^{-3}}$$

We will often find for particular systems that the pressure is related to the energy density mostly in a very simple way. For the ideal gas this is immediately clear: the pressure is the product of the particle density and the kinetic energy of the particles, i.e., the temperature. Therefore $p = \frac{2}{3}e$, where $e = \rho \langle E_{kin} \rangle$ is the (kinetic) energy density of the ideal gas.

Analogously to the temperature, the pressure also can be defined locally, i.e., in a small partial system. To measure the pressure one puts a small test area (unit area) into the system and measures the force which the system exerts on one side of the area. The other side of the test area has to be mechanically isolated from the system. On this side there may be a known reference pressure p_0. The pressure difference $p - p_0$ between the system's pressure and the internal pressure of the barometer causes an effective force which acts on the test area.

A central quantity of thermodynamics (and physics in general) is the *energy*. We are well acquainted with kinetic and potential energy from mechanics, as well as with electrical or magnetic energy from electrodynamics and with the chemical energy, which is also of electrical origin. In thermodynamics, only the total energy of a system, which is a macroscopic quantity, plays a role: the energy of a *single* particle has no meaning, but the *mean* energy per particle E/N is very important. Thermodynamics does not tell us how the total energy is distributed over the individual particles. As an example for the forms of energy mentioned above we will use the concept of work from mechanics in thermodynamic problems. We have

$$\delta W = -\vec{F}_i \cdot d\vec{s} \tag{1.18}$$

if $\vec{F}_i$ is the force exerted by the system and $d\vec{s}$ is a small line element. The minus sign in Equation (1.18) is purely convention in thermodynamics: we count energy which is added to a system as positive, and energy which is subtracted from a system as negative. As an example for work performed on a system we consider the compression of a gas against its internal pressure (Figure 1.5). In equilibrium, the external force $\vec{F}_a$ is just equal to the force $F_i = pA$ which is exerted by the pressure p on a piston with area A.

If one pushes the piston a distance $d\vec{s}$ further into the volume against the force exerted by the system, the amount of work needed is just

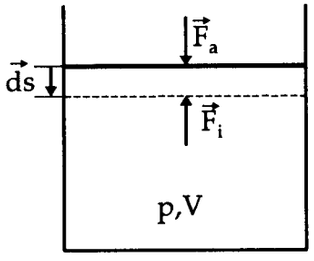

Figure 1.5. Concerning the compressional work.

$$\delta W = pA\,ds > 0 \tag{1.19}$$

since $d\vec{s}$ and $\vec{F}_i$ point in opposite directions. Now $A\,ds = -dV$ is just the decrease of the gas volume $dV < 0$ in the container, and we have

$$\delta W = -p\,dV \tag{1.20}$$

As one readily realizes, this equation also holds for an expansion. Note that we may only consider an infinitesimal amount of work, since the pressure changes during the compression. To calculate the total compressional work one needs an equation of state $p(V)$.

It is a general property of the energy added to or subtracted from a system that it is the product of an intensive state quantity (pressure) and the change of an extensive state

quantity (volume). We can illustrate this with further examples. If the system, for instance, contains an electric charge q, this charge gives rise to an electric potential ϕ. If one wants to add another charge dq with the same sign to the system, one has to perform an amount of work

$$\delta W = \phi \, dq \tag{1.21}$$

The locally defined electric potential is the intensive quantity which describes the resistance of the system against adding another charge, just as the pressure is the resistance against a compression. The sign in Equation (1.21) is caused by the fact that adding a positive charge while the potential is positive corresponds to work performed on a system.

If our thermodynamic system has an electric or magnetic dipole moment, adding another dipole to the system requires the work

$$\delta W_{el} = \vec{E} \cdot d\vec{D}_{el} \tag{1.22}$$

$$\delta W_{mag} = \vec{B} \cdot d\vec{D}_{mag} \tag{1.23}$$

Here the intensive field quantities are the electric and magnetic fields ($\vec{E}$ and $\vec{B}$), while $d\vec{D}$ denotes the change of the total dipole moment, which is an extensive quantity.

To complete our list of possible realizations of work we consider the work necessary to add another particle to a thermodynamic system. One might think that this does not require any work at all, but this is not the case. Our system should maintain equilibrium after adding the particle; therefore we cannot simply put the particle at rest into the system. Rather, it has to have a certain energy that is comparable to the mean energy of all the other particles. We define

$$\delta W = \mu \, dN \tag{1.24}$$

as the work necessary to change the particle number by dN particles. The intensive field quantity is called the *chemical potential* and represents the resistance of the system against adding particles. It is obvious that one can define and measure the chemical potential with the help of Equation (1.24) as well as one can measure the electric potential with Equation (1.21). If the system consists of several particle species, each species has its own chemical potential μ_i, and dN_i is the change in the particle number of species i. This is valid as long as the particle species do not interact with each other.

All different kinds of work have the generic property that they can be converted into each other without restrictions. For example, we can lift a weight with electrical energy or gain electrical energy from mechanical work with the help of a generator. There is no principle objection that these conversions do not proceed completely, i.e., with a rate of 100%, although real energy converters always have losses.

Heat and heat capacity

The situation is completely different with another kind of energy which is of principle importance for thermodynamics: heat. From the historical point of view R.J. Mayer (1842)

was the first to realize, after some fundamental considerations by Earl Rumfort (1798) and Davy (1799), that heat is a special form of energy. It is a daily experience that work performed on a system (of mechanical or electrical origin) often increases the temperature, and one can use this property to define an amount of heat. We therefore define

$$\delta Q = C\, dT \tag{1.25}$$

Here δQ is a small amount of heat which causes the increase dT in the temperature of a system. The constant of proportionality C is called *total heat capacity* of the system. To fix a unit for C we have to define a standard system. Formerly, one had the thermochemical *calorie* as the unit for heat; this is the amount of heat which warms 1g water from 14.5°C to 15.5°C. This corresponds to the definition $C_{1\,g\,H_2O,\,15°C} = 1$ cal/°C.

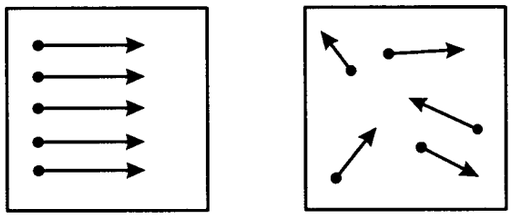

Figure 1.6. Particles with a) parallel and b) statistically distributed momenta.

By precise measurements Joule was able to show around 1843–49 that 1 cal of heat is equivalent to 4.184 Joule of mechanical work. By stirring, he conveyed an exactly defined amount of mechanical work to an isolated container of water, and measured the corresponding increase in temperature. Nowadays one produces a defined amount of heat mainly through the electrical resistance heater, which was also investigated by Joule. The SI unit for the heat capacity is also J/K.

The principle qualitative difference between work and heat is very simply explained in the microscopic picture. According to that picture, heat is energy which is statistically distributed over all particles. For instance, let us consider some particles with parallel (ordered) momenta which move in one direction. The kinetic energy of these particles can be completely regained at any moment and can be converted into other forms of energy, e.g., by decelerating the particles through a force. However, if the particles move in a completely disordered and statistical manner, it is obviously not possible to extract all the kinetic energy by a simple device. For instance if one exerts a force on the particles, like in Figure 1.6a, some particles would be decelerated and others would be accelerated, so that one cannot extract the total kinetic energy from the system.

It is therefore considerably simpler to change work into heat, which practically always happens by itself than to gain utilizable work from heat (here one always needs a thermodynamic engine). Here again the exceedingly large number of particles in macroscopic systems plays an important role. For instance, it might be possible to create, under certain circumstances, an appropriate (space-dependent) force field for the few particles in Figure 1.6b, with the property that it decelerates all particles, while the particles transfer their kinetic energy to the creating mechanism of the field. However, for 10^{23} particles this is unimaginable, and in the thermodynamic limit $N \to \infty$ it is impossible.

At this point we want to return once more to the heat capacity defined in connection with Equation (1.25). Obviously, the amount of heat δQ is an extensive quantity, therefore also the total heat capacity has to be an extensive quantity, since temperature is an intensive

variable. Thus, one can define an intensive quantity, the specific heat c, via

$$C = mc \tag{1.26}$$

with m being the mass of the substance. It is also possible to define the specific heat on a molar basis, $C = nc_{mol}$, with $n = N/N_A$. The quantity c_{mol} is the *molar specific heat.* When applying Equation (1.25), one has to take care of the fact that the heat capacity may depend on the external conditions under which heat is transferred to the system. It matters whether a measurement is performed at constant pressure or at constant volume. One respectively distinguishes c_V and c_p, the specific heats at constant volume and constant pressure, and denotes this by an index. Since we will investigate the relationship between c_V and c_p later on, we will now be content with noting that the definition $c_{H_2O} = 4.184\,\mathrm{J\,K^{-1}\,g^{-1}}$ holds at constant atmospheric pressure.

The equation of state for a real gas

As already mentioned, it is in general sufficient to fix a few state variables for a system. Then all other quantities assume values that depend on these state variables. We have encountered some examples:

$$pV = p_0 V_0, \qquad T = \text{const.} \tag{1.27}$$

or

$$V = \frac{T}{T_0} V_0, \qquad p = \text{const.} \tag{1.28}$$

As a standard example for a general equation of state which connects all relevant variables, we have the ideal gas law

$$pV = NkT \tag{1.29}$$

which is, however, valid only for dilute gases (low pressure). Measuring the pressure of an ideal gas at constant temperature, particle number and volume, we can determine the value of Boltzmann's constant with the help of Equation (1.29). In most cases one takes $N = N_A$ particles, i.e., just one mole, and obtains

$$N_A k = R = 8.31451\,\mathrm{J\,K^{-1}\,mol^{-1}} \tag{1.30}$$

The constant $N_A k = R$ is named the *gas constant.*

In thermodynamics one often assumes equations of state to be polynomials of a variable. If Equation (1.29) is correct for low pressures ($p \approx 0$), the ansatz

$$pV = NkT + B(T)p + C(T)\,p^2 + \cdots \tag{1.31}$$

should be a more sophisticated equation of state for larger pressures. As a first approximation terminates the *virial expansion* Equation (1.31)) after the linear term; the coefficient $B(T)$ can be determined experimentally. The quantity $B(T)$ is called the first *virial coefficient.*

If one does not expand the equation of state of a real gas in terms of low pressure, but rather in terms of low density, one obtains an analogous equation,

$$pV = NkT + B'(T)\frac{N}{V} + C'(T)\left(\frac{N}{V}\right)^2 + \cdots \tag{1.32}$$

which is often also called the virial expansion. Figure 1.8 shows that many gases are described by the same virial coefficient, scaled to the main characteristic quantities of the interaction potential U_0 between the particles. These characteristic quantities are the range of interaction r_0, and the depth of the potential. Two possible forms of the potential between the atoms of, e.g., rare gases are illustrated in Figure 16.2. The potential vanishes for large interparticle distances; hence all these gases resemble an ideal gas for low densities (large mean particle distance). For medium distances ($\simeq r_0$) the potential has an attractive region, while it is strongly repulsive for small distances. This repulsion is caused by a large overlap of the atomic electron clouds, as long as a chemical bond between these atoms is not possible (no mutual molecular orbits). Thus, one can assume the atoms to be approximately hard spheres with a certain proper volume, which is given by the (mean) radii of their electron clouds. Beyond this region, however, the atoms feel an attractive force (van der Waals interaction). Therefore, so-called simple gases (namely those for which our schematic interaction is a good approximation, like Ar, N_2, etc.) show quite similar behavior. Differences are only due to the different sizes of the atoms (measured in terms of r_0) and the different strengths of the interaction (measured in terms of U_0). Since the first virial coefficient has the dimension of a volume, one should obtain similar curves for all gases, if one plots $B(T)$ in units of the atomic or molecular proper volume, $\sim r_0^3$, and if one plots the temperature, which is closely related to the kinetic energy of the particles, in units of the potential depth U_0. Figure 1.8 shows that these considerations are indeed correct. Also shown is a numerical calculation of the virial coefficient, performed via methods of statistical mechanics (cf. Chapter 16) for a Lennard–Jones potential. The parameters r_0 and U_0 of the potential are fitted to obtain optimum agreement with the data.

Another well-known equation of state for real gases is the equation of van der Waals (1873), which is made plausible by the following consideration: Equation (1.29) neglects the proper volume of the particles, which causes $V \to 0$ for $T \to 0$. We can mend this if we substitute for V the quantity $V - Nb$, where b is a measure for the proper volume of a particle. Furthermore, in an ideal gas one neglects the interaction between the particles, which is mainly attractive. Let us, for instance, consider a globe containing a gas with a particle density N/V. Inside the globe, the forces acting between the particles will be zero on the average.

On the other hand, the particles on the surface feel an effective force in the direction of the interior of the globe. This means that the pressure of a real gas has to be smaller than that of an ideal gas. We can account for this in Equation (1.29) if we substitute the ideal gas pressure p_{id} by $p_{real} + p_0$, where p_0 is the so-called inner pressure. (See Figure 1.7.)

With $p_{id} = p_{real} + p_0$, it is obvious that the pressure of a real gas is smaller by p_0 than that of the ideal gas. The inner pressure p_0 is, however, not simply a constant, but depends on the mean distance between the particles and on how many particles are on the surface.

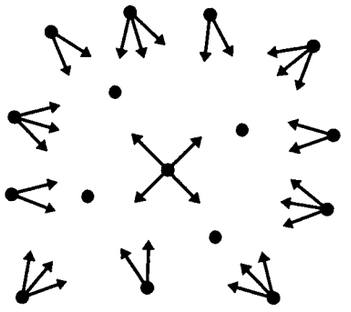

Figure 1.7. Concerning the inner pressure.

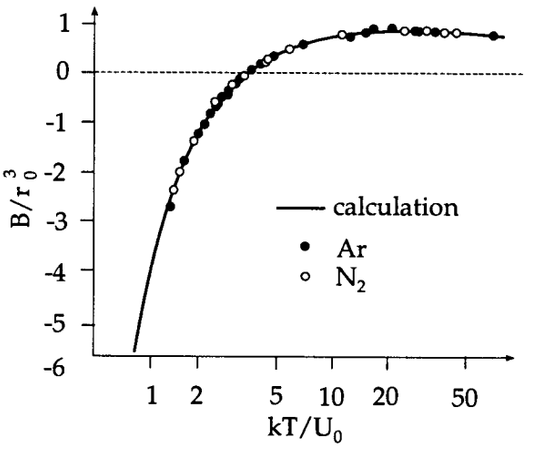

Figure 1.8. Virial coefficients of various gases.

Both dependences are in crude approximation proportional to the particle density N/V, so that $p_0 = a(N/V)^2$, where a is a constant.

Van der Waals' equation therefore reads

$$\left(p + \left(\frac{N}{V}\right)^2 a\right)(V - Nb) = NkT \tag{1.33}$$

Here a and b are material constants, which are mostly cited per mole and not per particle. Note that equations of state do not require any justification in thermodynamics! Solely decisive is the fact whether and in which region of the state quantities an equation of state yields an appropriate description of the behavior of a system.

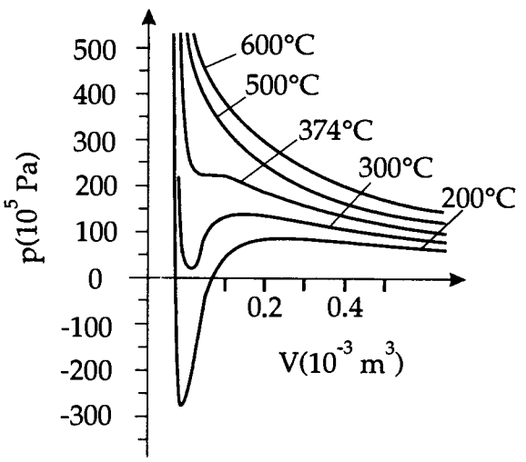

Figure 1.9. Van der Waals isotherms in the pV–diagram.

In Figure 1.9 the pressure is shown as a function of the volume for T = const. according to Equation (1.33). The best parameters a and b for water are taken. Obviously, there is an error: for small temperatures and certain volumes the pressure becomes negative. This means that the inner pressure is too large in these regions. Furthermore, also for positive pressures there are regions where the pressure decreases with decreasing volume, i.e., where the system cannot be stable, but wants to compress itself spontaneously to a smaller volume.

As we will see, the equation of state (1.33) is nevertheless much better than it may seem on first sight, if one additionally regards the gas-liquid phase transition.

For high temperatures and low densities, van der Waals' equation becomes the equation for the ideal gas. Typical values for the constants a and b are given in Table 1.1.

As one notes, the proper volume b is a very small correction to the molar volume $22.4 \cdot 10^{-3}$ m^3/mol of an ideal gas at 0°C.

TABLE 1.1 Parameters of van der Waals' equation of state

Material	a(Pa m^6 mol^{-2})	$b(10^{-3}$m^3 mol^{-1})
H_2	0.01945	0.022
H_2O	0.56539	0.031
N_2	0.13882	0.039
O_2	0.13983	0.032
CO_2	0.37186	0.043

An often used approximation for van der Waals' equation is obtained by setting N/V in the inner pressure equal to that of an ideal gas, $N/V \approx p/kT$. Then it holds that

$$\left(p + \frac{p^2}{(kT)^2}a\right)(V - Nb) = NkT \tag{1.34}$$

or

$$pV = \frac{NkT}{1 + \frac{pa}{(kT)^2}} + pNb \tag{1.35}$$

For low pressures and high temperatures we have $pa/(kT)^2 \ll 1$ and we can expand the denominator, with the result

$$pV = NkT + N\left(b - \frac{a}{kT}\right)p + \cdots \tag{1.36}$$

As we observe, van der Waals' equation can also be expressed by the virial expansion, with $B(T) = N[b - a/(kT)]$. If one compares this first virial coefficient with the measurements of Figure 1.8, one finds indeed a satisfying agreement. For high temperatures the virial coefficient determined from van der Waals' equation approaches the constant value b, which determines the proper volume of the particles. For $kT = a/b$, $B(T) = 0$, and for small temperatures ($kT \to 0$), $B(T)$ becomes strongly negative. Van der Waals' equation yields also higher order virial coefficients ($C(T) \neq 0$, etc.) in the virial expansion for low pressures.

Specific heat

In the following, we want to investigate the specific heat in more detail. As mentioned in the last section in context with its definition, the specific heat depends on the external conditions under which an amount of heat is transferred to the system. If this happens at constant pressure (e.g., atmospheric pressure) one obtains c_p, while c_V is measured at constant volume. The specific heats c_V as well as c_p can be considered functions of the state variables T and p, which are the most easy to control experimentally. For dilute gases ($p \to 0$), the specific heats are mainly independent of pressure and even approximately independent of temperature (at least for rare gases, cf. Figure 1.10).

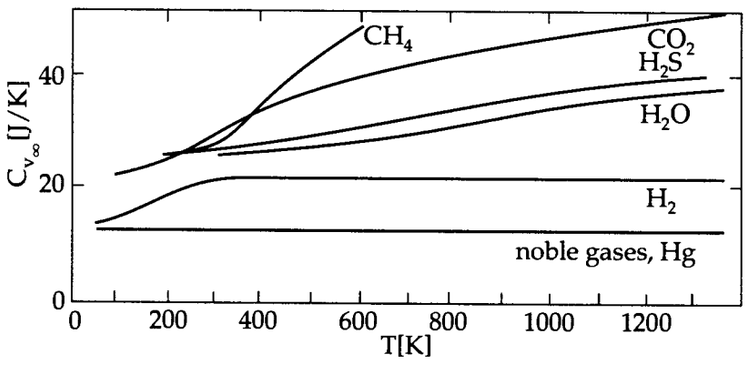

Figure 1.10. Specific heat at constant volume for low pressure.

If one interprets the specific heat as the ability of a substance to absorb energy in a statistically distributed way, it becomes clear that this ability increases with the number of degrees of freedom of a particle. For instance, particles in monatomic rare gases have only the possibility of translatory motion, while those in biatomic gases are also able to rotate. Polyatomic gases have still more degrees of freedom, e.g., those of oscillation of the particles relative to each other. If the pressure is no longer low, the specific heats become also pressure dependent. As an example we show the behavior of c_p and c_V for ammonia in Figure 1.11. The saturation line corresponds to the gas $\rightarrow$ liquid phase transition.

At first one realizes, on inspecting Figure 1.11, that the specific heat at constant pressure c_p, is always larger than that at constant volume c_V. If one adds a certain amount of heat δQ to a system at constant pressure, the system will not only heat up, but in general also will expand, and thus it will perform volume work against the external pressure (atmospheric pressure). The amount of heat added is therefore not only stored in the gas in the form of statistically distributed kinetic and potential energy, but is also required to perform work against the external pressure. Thus, a system can in general store a larger amount of heat at constant pressure than at constant volume ($c_p > c_V$). A generally valid relationship between c_p and c_V will be derived in Example 4.12.

Furthermore, the figure tells us that c_p and c_V increase strongly, if one approaches the phase transition from gaseous to liquid ammonia (saturation line) at constant pressure and decreasing temperature. A (strong) increase of the specific heat (or a divergence) as a function of temperature is a general sign for the onset of phase transitions. Further examples will prove this (cf., e.g., the figures in Chapter 17).

The specific heats (c_p and c_V) increase also (continuously) with increasing pressure. The nearer they approach each other on average (high pressure, high density), the stronger are the forces between the particles of the gas. A part of the heat added is then also stored in the form of potential energy (not only as kinetic energy of the particles), which effects a larger specific heat at high densities (high pressures).

For liquids and solids one almost always quotes the value of c_p which is easier to measure. While liquids show quite different dependences on pressure and temperature (except, e.g., Hg and H_2O, with $c_p \approx$ const.), for metals the law of Dulong and Petit (1819) holds. According to this law, all metals have the constant specific heat $c_p = 25.94\,\mathrm{J\,K^{-1}\,mol^{-1}}$ over a wide range of temperatures. The specific heat is in general of great

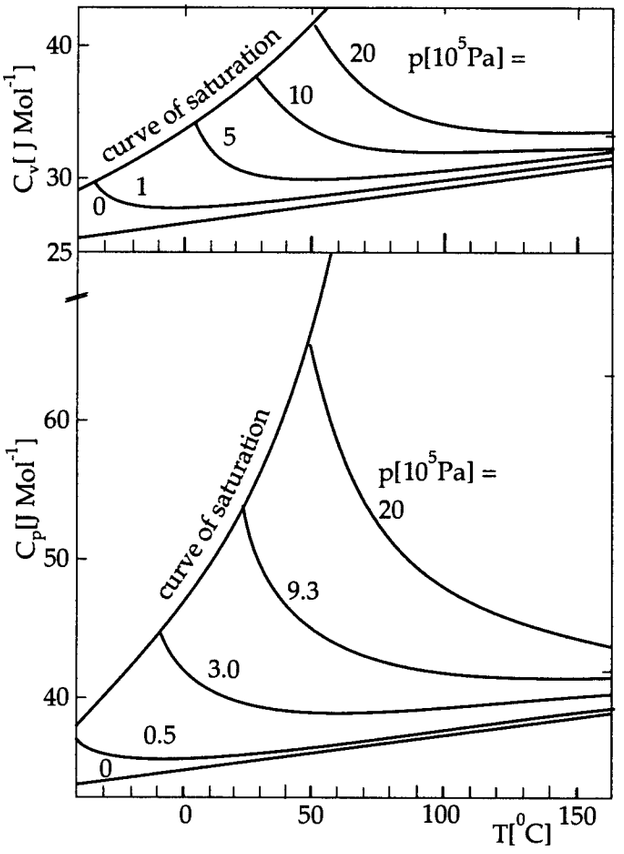

Figure 1.11. Specific heats c_p and c_V of ammonia.

importance in thermodynamics, since it is easy to measure and allows for the calculation of a lot of other properties. Furthermore, the precise measurement of specific heats at very low temperatures has shown that many properties of matter can only be understood with the help of quantum mechanics and quantum statistics, respectively. Thus, we will have to consider the specific heat quite frequently in the following.

Finally we investigate an equation of state corresponding to an ideal gas equation for solids. In this case, the temperature and pressure dependence of the volume is given in a range of values by

$$V(T, p) = V_0\{1 + \alpha(T - T_0) - \kappa(p - p_0)\} \tag{1.37}$$

i.e., by a linear approximation. Here $V(T_0, p_0) = V_0$ is an arbitrary initial state. The constants α and κ,

$$\alpha = \frac{1}{V_0}\frac{\partial V}{\partial T}\bigg|_{p=p_0} \tag{1.38}$$

$$\kappa = -\frac{1}{V_0}\frac{\partial V}{\partial p}\bigg|_{T=T_0} \tag{1.39}$$

are called the *coefficient of expansion* (at constant pressure) and the *compressibility* (at constant temperature), respectively.

The coefficient of expansion of many materials is of the order of $\alpha \approx 10^{-5}\ \mathrm{K}^{-1}$, while the compressibility is of the order of $\kappa \approx 10^{-11}\ \mathrm{Pa}^{-1}$. This has the consequence that even small changes in the temperature at given constant volume may effect a very high pressure, i.e. large forces.

Changes of state—reversible and irreversible processes

It is a daily experience that a process in an isolated system proceeds by itself until an equilibrium state is reached. Since such processes do not reverse themselves, they are called *irreversible*. Examples of such processes are nearly all processes of daily life, in particular the expansion of a gas from a smaller into a larger volume or all processes which produce friction heat. For instance, a pendulum without a driving force will by itself cease to swing after some time, since its mechanical energy is transformed into heat by friction. The reverse process, that a pendulum starts to swing by itself while the surroundings cool, has never been observed. It is characteristic for irreversible processes that they proceed over nonequilibrium states.

On the other hand, processes which proceed only over equilibrium states are called *reversible*. A reversible process is an idealization which is, strictly speaking, nonexistent, for if a system is in an equilibrium state, the variables of state have time-independent values and nothing happens. Reversible changes of state, however, can be simulated by small (infinitesimal) changes of the variables of state, where the equilibrium state is only slightly disturbed, if these changes happen sufficiently slowly compared to the relaxation time of the system. Such changes of state are also called *quasi reversible*. The importance of reversible changes of state is the following: for every small step of the process the system is in an equilibrium state with definite values of the state quantities, so that the total changes of the state variables can be obtained by integrating over the infinitesimal reversible steps. For irreversible processes this is not possible. During an irreversible process it is in general not possible to attribute values to the state quantities.

Example 1.3: Isothermal expansion

We consider the expansion of a gas at constant temperature (*isothermal expansion*, see Figure 1.12). A constant temperature is practically realized by a *heat bath*, e.g., by a large vessel with water of a temperature T, which is attached to the system and which is in thermal equilibrium with the system.

We can simply accomplish the isothermal expansion of the gas from the volume V_1 to V_2 by removing the external force F_a which acts on the piston and maintains equilibrium. Thus, the gas will rapidly expand up to the volume V_2, while during this process local pressure differences, turbulence, as well as temperature and density gradients will occur.

This process happens by itself and would never reverse itself. Therefore it is irreversible.

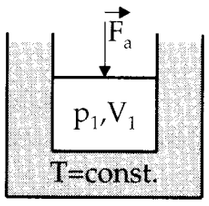

Figure 1.12. Isothermal system.

During the expansion we cannot ascribe values to the macroscopic state quantities. We can do this only after an equilibrium state is reestablished. The work performed by the expansion of the system is zero as long as one uses an ideal massless piston.

However, we can also perform this isothermal expansion reversibly, or at least quasi reversibly, if we decrease the force at each step only by an infinitesimal amount and wait for the establishment of equilibrium in the new situation. The length of this waiting period depends on the relaxation time of the system. The major differences with the irreversible (isothermal) expansion are that in this case the thermodynamic variables have definite values for each intermediate step and that, for instance, the equation of state is applicable. If we consider an ideal gas in our case, we have $p = NkT/V$, and we can calculate the total amount of work performed in the expansion of the system,

$$\int_1^2 dW = -\int_{V_1}^{V_2} p\,dV = -NkT\int_{V_1}^{V_2}\frac{dV}{V} = -NkT\ln\frac{V_2}{V_1} \tag{1.40}$$

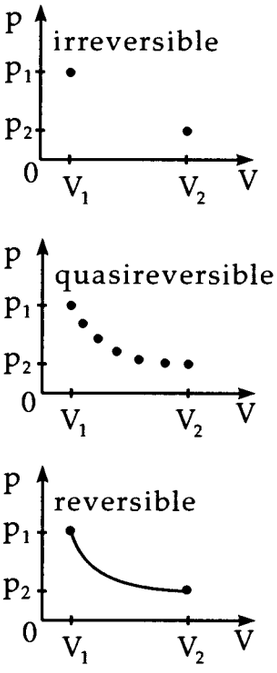

Figure 1.13. Different ways to perform a process.

Contrary to the irreversible expansion, our system has now done work against the external force F_a. We note that this reversible work of the system is the maximum work that can be extracted from the system: there is no way to gain more work from a system than reversible work.

Real expansions, of course, lie between the extreme cases of the completely irreversible expansion ($\Delta W = 0$) and the completely reversible expansion ($\Delta W = -NkT\ln(V_2/V_1)$). The reversible and irreversible processes of our example are illustrated in Figure 1.13.

In the irreversible case we can determine only the initial and final states, while all points of the pV-isotherm are attained during the reversible process. Although the initial and final states are identical for the reversible and irreversible process, the performed work (energy balance) is completely different. Obviously, the irreversible process wastes work. By the way, this is also the case if we consider isothermal compression. For a reversible process we need in this case the work

$$\int_2^1 dW = -\int_{V_2}^{V_1} p\,dV = -NkT\ln\frac{V_1}{V_2} = NkT\ln\frac{V_2}{V_1} > 0$$

Here it is assumed that in each step the force exerted on the piston is only infinitesimally increased. If we instead push the piston spontaneously with large effort, we have to spend more work, which is consumed in turbulences and finally transferred to the heat bath in the form of heat.

As we see from this example, the work performed in the isothermal expansion depends on the way in which the process is carried out, although the initial and final states are the same in both cases. This is a special case of the daily experience that the work performed in a process, and also the transferred heat, not only depends on the initial and final state of the system, but also on the way of performing the process. This, however, means that work and heat are not suited to describing a macroscopic state in a unique way. They are

not state quantities! Mathematically, this means that work and heat are not exact (i.e., total) differentials. We will investigate this problem in detail in the next section.

If one considers a state quantity as a function of certain variables of state (e.g., T, p, etc.), one speaks of a state function. As experience shows, the number of variables of state which are necessary to uniquely determine a state, depends on the possible kinds of energy which the system can absorb or emit. For many systems these are, for instance, heat δQ and mechanical work δW_{mech}, as well as chemical energy δW_{chem}. To any of these kinds of energy belongs a variable of state (e.g., T, V or N), and it is sufficient to determine these three quantities to fix all other state quantities. However, if the system consists of various particle species, a separate particle number belongs to each particle species. We will discuss this problem in detail when we study the thermodynamic laws and Gibbs' phase rule.

In the next section we want to investigate some generic properties of state functions, and we will restrict ourselves to functions of two state variables, for example,

$$z = f(x, y) \tag{1.41}$$

It is often impossible to solve an equation of state for a certain quantity, and one has to be content with an implicit equation:

$$f(x, y, z) = 0 \tag{1.42}$$

It is characteristic of state quantities, and hence of state functions, that they depend only on the values of the state variables, but not on the way (i.e., on the procedure) in which these values are assumed. If one changes the state variables by dx and dy with respect to the initial values x and y, as is done in reversible changes of state, for the change of z we have

$$dz = \left.\frac{\partial f(x, y)}{\partial x}\right|_y dx + \left.\frac{\partial f(x, y)}{\partial y}\right|_x dy \tag{1.43}$$

It is common practice in thermodynamics to denote fixed variables in the partial differentiation in the form $|_x$ or $|_y$. One should always do this carefully since y and x are often not independent from each other, but are related by the laws of thermodynamics.

Exact and inexact differentials, line integrals

We start from a state function

$$z = f(x, y) \tag{1.44}$$

with the differential

$$dz = \left.\frac{\partial f(x, y)}{\partial x}\right|_y dx + \left.\frac{\partial f(x, y)}{\partial y}\right|_x dy \tag{1.45}$$

We now introduce a more general and mathematically convenient notation. Equation (1.45) can namely also be interpreted as a scalar product of the gradient of f with the vector $\binom{dx}{dy} = d\vec{x}$, and be written in the form

$$df(\vec{x}) = \nabla f(\vec{x}) \cdot d\vec{x} \tag{1.46}$$

A property of such total differentials which has enormous importance for thermodynamics, is that the corresponding original function (state function) can be obtained, up to an additive constant, via line integration along an *arbitrary* curve.

$$f(\vec{x}) - f_0(\vec{x}_0) = \int_C \nabla f(\vec{x}) \cdot d\vec{x} \tag{1.47}$$

The curve C leads from $\vec{x}_0 = \binom{x_0}{y_0}$ to $\vec{x} = \binom{x}{y}$. If $\vec{x}(t)$ with $t \in [0, 1]$ is a parametric representation of this curve, the explicit calculation is done via

$$f(\vec{x}) - f_0(\vec{x}_0) = \int_0^1 dt\, \nabla f(\vec{x}(t)) \cdot \frac{d\vec{x}(t)}{dt} \tag{1.48}$$

Here the integrand is only a function of the parameter t. Now the question is when a given differential is total, or equivalently, under what conditions the integration in Equations (1.47) or (1.48) does not depend on the integration contour. This is no trivial matter, of course, as we have already seen in considering the work δA, which is not a total differential. By the way, the problem connected with Equations (1.47) and (1.48) is already known from classical mechanics, where we use the same formalism to calculate work! There, however, work is a total differential, in contrast to thermodynamics, as long as the force can be deduced from a potential via $\vec{F} = -\nabla V(\vec{r})$. The existence of a potential is, in the mathematical sense, necessary and sufficient for Equation (1.47) to be independent of the integration contour. If an arbitrary differential $\vec{F}(\vec{x}) \cdot d\vec{x}$ is given, this differential is complete (or total), if $\vec{F}(\vec{x}) = \nabla f(\vec{x})$ for a potential $f(\vec{x})$. The existence of a potential is still not a very practical criterion on which to decide whether a given differential is complete. However, from classical mechanics we know a simple condition for deciding whether a force possesses a potential. It is necessary and sufficient that

$$\nabla \times \vec{F} = \vec{0} \tag{1.49}$$

or

$$\frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z} = 0, \quad \frac{\partial F_x}{\partial z} - \frac{\partial F_z}{\partial x} = 0, \quad \frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = 0 \tag{1.50}$$

If $\vec{F} = \nabla f$ is valid, Equations (1.50) reduce to

$$\frac{\partial^2 f}{\partial y \partial z} - \frac{\partial^2 f}{\partial z \partial y} = 0, \quad \frac{\partial^2 f}{\partial z \partial x} - \frac{\partial^2 f}{\partial x \partial z} = 0, \quad \frac{\partial^2 f}{\partial x \partial y} - \frac{\partial^2 f}{\partial y \partial x} = 0 \tag{1.51}$$

This, however, means nothing else than the right to interchange the sequence of differentiation, which holds certainly for a function $f(x, y, z)$ which is totally differentiable. Thus, if a differential $\vec{F} \cdot d\vec{x}$ is given (with an arbitrary number of variables), we only have to prove the validity of Equation (1.50) to know whether the differential is exact.

Example 1.4: A simple differential

Consider the differential

$$\vec{F} \cdot d\vec{x} = yx\, dx + x^2\, dy$$

It is not exact, since then

$$\frac{\partial F_x}{\partial y} - \frac{\partial F_y}{\partial x} = \frac{\partial (yx)}{\partial y} - \frac{\partial x^2}{\partial x} = x - 2x = -x \tag{1.52}$$

should vanish, which is not the case. However,

$$\vec{F} \cdot d\vec{x} = y\,dx + x\,dy \tag{1.53}$$

is exact, since

$$\frac{\partial F_x}{\partial y} - \frac{\partial F_y}{\partial x} = \frac{\partial y}{\partial y} - \frac{\partial x}{\partial x} = 0$$

In this case we can calculate the function whose (total) differential is given by Equation (1.53). To this end we integrate along the contour

$$C_1 = \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{pmatrix} x_0 + t(x - x_0) \\ y_0 + t(y - y_0) \end{pmatrix} \qquad t \in [0, 1]$$

and we have, according to Equation (1.48),

$$\begin{aligned} & f(x, y) - f_0(x_0, y_0) \\ &= \int_0^1 dt\{(y_0 + t(y - y_0))(x - x_0) \\ &\quad + (x_0 + t(x - x_0))(y - y_0)\} \\ &= y_0(x - x_0) + \frac{1}{2}(y - y_0)(x - x_0) \\ &\quad + x_0(y - y_0) + \frac{1}{2}(x - x_0)(y - y_0) \\ &= xy - x_0 y_0 \end{aligned} \tag{1.54}$$

By differentiating we readily confirm that

$$\left.\frac{\partial f}{\partial x}\right|_y = y \qquad \text{and} \qquad \left.\frac{\partial f}{\partial y}\right|_x = x$$

Now we show that the same result is obtained via another curve C_2. (See Figure 1.14.) Thus, let

$$C_2 = \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{cases} \begin{pmatrix} t \\ y_0 \end{pmatrix} & t \in [x_0, x] \\ \begin{pmatrix} x \\ t \end{pmatrix} & t \in [y_0, y] \end{cases}$$

where we have to add the integrals over both parts of the curve (the parameter t has not necessarily to be normalized on (0, 1)):

$$f(x, y) - f_0(x_0, y_0) = \int_{x_0}^{x} dt(y_0 \cdot 1 + t \cdot 0) + \int_{y_0}^{y} dt(t \cdot 0 + x \cdot 1)$$
$$= y_0(x - x_0) + x(y - y_0)$$
$$= xy - x_0y_0$$

where $\frac{dx(t)}{dt} = 1$, $\frac{dy(t)}{dt} = 0$ on part 1 and $\frac{dx(t)}{dt} = 0$, $\frac{dy(t)}{dt} = 1$ on part 2.

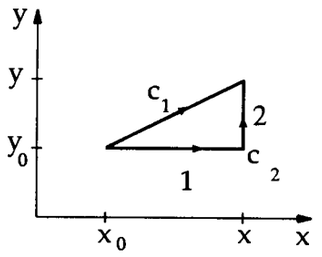

Figure 1.14. Representation of the integration contours.

As one notices, the result is identical with Equation (1.54). For many practical cases the curve C_2 is very convenient. It is possible to construct an exact differential from a nonexact differential $\vec{F}(\vec{x}) \cdot d\vec{x}$ by multiplication with an appropriate function $g(\vec{x})$. The determination of the function $g(\vec{x})$, however, requires the solution of a system of partial differential equations. Let $g(\vec{x})\vec{F}(\vec{x}) \cdot d\vec{x}$ be the corresponding total differential. Then we have (cf. Equation (1.50)) for n variables:

$$\frac{\partial}{\partial x_i}(g(\vec{x})F_k(\vec{x})) = \frac{\partial}{\partial x_k}(g(\vec{x})F_i(\vec{x}))$$
$$i, k = 1, 2, \ldots, n \qquad \textbf{(1.55)}$$

For a given $\vec{F}(\vec{x})$, these are determining equations for the unknown function $g(\vec{x})$. One calls $g(\vec{x})$ the *integrating factor*.

Example 1.5: The integrating factor

Again, let the differential from Example 1.4 be given,

$$\vec{F} \cdot d\vec{x} = yx\,dx + x^2\,dy$$

We now try to determine $g(x, y)$ in such a way that

$$g\vec{F} \cdot d\vec{x} = g(x, y)yx\,dx + g(x, y)x^2\,dy$$

is an exact differential. Then it would hold that

$$\frac{\partial}{\partial x}(g(x, y)x^2) = \frac{\partial}{\partial y}(g(x, y)xy) \qquad \textbf{(1.56)}$$

Here the system of Equations (1.55) reduces to a single partial differential equation for $g(x, y)$. We try to solve this via the product ansatz $g(x, y) = g_1(x)g_2(y)$. If we insert this in Equation (1.56), it follows that

$$2xg_1(x)g_2(y) + x^2g_2(y)\frac{dg_1(x)}{dx}$$
$$= xg_1(x)g_2(y) + xyg_1(x)\frac{dg_2(y)}{dy}$$

If we divide this equation by $xg_1(x)g_2(y) \neq 0$, it follows after rearranging terms that

$$1 + \frac{x}{g_1(x)}\frac{dg_1(x)}{dx} = \frac{y}{g_2(y)}\frac{dg_2(y)}{dy} \tag{1.57}$$

Here we have achieved a complete separation of the variables x and y. We may now argue that Equation (1.57), which should be valid for all combinations x and y, is fulfilled only if both sides of the equation have constant values, i.e., if

$$1 + \frac{x}{g_1(x)}\frac{dg_1(x)}{dx} = C = \frac{y}{g_2(y)}\frac{dg_2(y)}{dy}$$

Each of these equations is readily solved. From

$$\frac{d \ln g_1(x)}{dx} = \frac{C-1}{x} \quad \text{and} \quad \frac{d \ln g_2(y)}{dy} = \frac{C}{y}$$

it follows that

$$\ln g_1(x) = (C-1)\ln x + K_1 \quad \text{and} \quad \ln g_2(y) = C \ln y + K_2$$

or

$$g(x, y) = g_1(x)g_2(y) = x^{C-1}y^C K, \quad K = e^{K_1+K_2}$$

where the constants C, K_1 and K_2 are arbitrary. Since we only want to determine one special function $g(x, y)$, we may choose $C = 0$, $K_1 = -K_2$, i.e., $g(x, y) = x^{-1}$. Thus our differential is now

$$g\vec{F} \cdot d\vec{x} = \frac{1}{x}(xy\,dx + x^2\,dy) = y\,dx + x\,dy$$

This is just the differential of Equation (1.53), which we already know to be an exact differential.

Exercise 1.6: Exact and inexact differentials

Consider the differential

$$\vec{F} \cdot d\vec{x} = (x^2 - y)\,dx + x\,dy \tag{1.58}$$

Is it exact? Calculate $\int_{C_i} \vec{F} \cdot d\vec{x}$ where C_i are the contours from (1, 1) to (2, 2) in Figure 1.15. If it is not an exact differential, what is the integrating factor? Determine the original function.

Solution If the differential (1.58) were exact,

$$\frac{\partial F_x}{\partial y} - \frac{\partial F_y}{\partial x} = \frac{\partial(x^2 - y)}{\partial y} - \frac{\partial x}{\partial x} = -2$$

would necessarily vanish, which is not the case. Therefore it is not an exact differential. We calculate the integrals $\int_{C_i} \vec{F} \cdot d\vec{x}$ as line integrals with an appropriate parametrization:

$$\int_C \vec{F}(\vec{x}) \cdot d\vec{x} = \int_0^1 dt \left\{ (x^2(t) - y(t))\frac{dx(t)}{dt} + x(t)\frac{dy(t)}{dt} \right\}$$

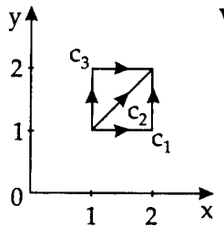

Figure 1.15. Representation of the integration contours.

We use

$$C_1 = \begin{cases} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 2t+1 \\ 1 \end{pmatrix} & t \in \left[0, \frac{1}{2}\right] \\ \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 2 \\ 2t \end{pmatrix} & t \in \left[\frac{1}{2}, 1\right] \end{cases} \tag{1.59}$$

The corresponding line integral reads

$$\begin{aligned} \int_{C_1} \vec{F}(\vec{x}) \cdot d\vec{x} &= 2 \int_0^{1/2} dt((2t+1)^2 - 1) + \int_{1/2}^1 dt 2 \cdot 2 \\ &= \left(\frac{1}{3} + 1\right) + 2 \\ &= \frac{10}{3} \end{aligned}$$

For the curve C_2 we analogously have

$$C_2 = \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} t+1 \\ t+1 \end{pmatrix} \quad t \in [0, 1] \tag{1.60}$$

The integral reads

$$\begin{aligned} \int_{C_2} \vec{F}(\vec{x}) \cdot d\vec{x} &= \int_0^1 dt\{((t+1)^2 - t - 1) \cdot 1 + (t+1) \cdot 1\} \\ &= \int_0^1 dt(t+1)^2 \\ &= \frac{7}{3} \end{aligned}$$

Finally, the curve C_3 is given by

$$C_3 = \begin{cases} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 1 \\ 2t+1 \end{pmatrix} & t \in \left[0, \frac{1}{2}\right] \\ \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 2t \\ 2 \end{pmatrix} & t \in \left[\frac{1}{2}, 1\right] \end{cases} \tag{1.61}$$

and the integral along this curve is

$$\begin{aligned} \int_{C_3} \vec{F}(\vec{x}) \cdot d\vec{x} &= \int_0^{1/2} dt 2 \cdot 1 + \int_{1/2}^1 dt((2t)^2 - 2) \cdot 2 \\ &= -1 + 8 \int_{1/2}^1 t^2 dt \\ &= \frac{4}{3} \end{aligned}$$

All three curves yield, as expected, different values for the integral, since the differential is not exact. We now try to determine the integrating factor. If we denote it by $g(x, y)$, it must hold that

$$\frac{\partial}{\partial y}\left((x^2 - y)g(x, y)\right) - \frac{\partial}{\partial x}\left(xg(x, y)\right) = 0$$

We will try the product ansatz $g(x, y) = g_1(x)g_2(y)$. This leads to

$$(x^2 - y)g_1(x)\frac{dg_2(y)}{dy} - xg_2(y)\frac{dg_1(x)}{dx} = 2g_1(x)g_2(y)$$

or after division by $g_1(x)g_2(y) \neq 0$ ($g(x, y)$ is assumed to be nonzero, otherwise it would be a trivial integrating factor),

$$(x^2 - y)\frac{d}{dy}\ln g_2(y) - x\frac{d}{dx}\ln g_1(x) = 2$$

The derivative of $\ln(g_2(y))$ has to vanish, since there is otherwise no possibility to choose functions g_1 and g_2, so that the lefthand side equals the righthand side for arbitrary x and y. The reader may confirm this fact by distinguishing between all possible cases. The second term depends only on x, and on the right we have a constant. It follows that

$$\frac{d}{dx}\ln g_1(x) = -\frac{2}{x} \Rightarrow g_1(x) = \frac{1}{x^2}$$

while $g_2(y) = 1$, and therefore one may choose $\ln(g_2(y)) = 0$. Hence we have found $g(x, y) = x^{-2}$. Indeed,

$$g\vec{F} \cdot d\vec{x} = \left(1 - \frac{y}{x^2}\right)dx + \frac{1}{x}\,dy \qquad \textbf{(1.62)}$$

is an exact differential because of

$$\frac{\partial}{\partial y}\left(1 - \frac{y}{x^2}\right) = -\frac{1}{x^2} \qquad \text{and} \qquad \frac{\partial}{\partial x}\left(\frac{1}{x}\right) = -\frac{1}{x^2}$$

We now show that the integrals $\int_C g\vec{F} \cdot d\vec{x}$ have the same value for all integrations contours. With the parametrizations of Equations (1.59–61), it follows that

$$\begin{aligned}\int_{C_1} g\vec{F} \cdot d\vec{x} &= \int_0^{1/2}\left(1 - \frac{1}{(2t+1)^2}\right)2\,dt + \int_{1/2}^{1}\frac{1}{2}\cdot 2\,dt \\ &= \frac{3}{2} - \int_0^{1/2}\frac{2\,dt}{(2t+1)^2} \\ &= \frac{3}{2} - \frac{1}{2} = 1\end{aligned}$$

and also that

$$\int_{C_2} g\vec{F} \cdot d\vec{x} = \int_0^1 \left\{\left(1 - \frac{1}{t+1}\right) + \frac{1}{t+1}\right\}dt = 1$$

and

$$\int_{C_3} g\vec{F}\cdot d\vec{x} = \int_0^{1/2} 1\cdot 2\,dt + \int_{1/2}^{1}\left(1-\frac{2}{(2t)^2}\right)2\,dt$$
$$= 2 - \int_{1/2}^{1}\frac{dt}{t^2}$$
$$= 2+1-2 = 1$$

That is, along the contours C_1, C_2 and C_3 (and along all others), one obtains the same value. There exists a primitive function, which we now want to determine. We integrate, starting from any initial point (x_0, y_0) to the final point (x, y) along the most convenient path:

$$C = \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{pmatrix} t \\ \dfrac{y-y_0}{x-x_0}(t-x_0)+y_0 \end{pmatrix} \quad t\in[x_0, x]$$

and we obtain for the primitive function $f(x, y) - f_0(x_0, y_0) = \int_C g\vec{F}(\vec{x})\cdot d\vec{x}$

$$f(x,y)-f_0(x_0,y_0) = \int_{x_0}^{x} dt\left\{1-\frac{1}{t^2}\left(\frac{y-y_0}{x-x_0}(t-x_0)+y_0\right)+\frac{1}{t}\frac{y-y_0}{x-x_0}\right\}$$
$$= \int_{x_0}^{x} dt\left\{1+\frac{1}{t^2}\left(\frac{y-y_0}{x-x_0}x_0-y_0\right)\right\}$$
$$= x-x_0-\left(\frac{y-y_0}{x-x_0}x_0-y_0\right)\left(\frac{1}{x}-\frac{1}{x_0}\right)$$
$$= x-x_0+\left(\frac{(y-y_0)x_0-y_0(x-x_0)}{x-x_0}\frac{x-x_0}{xx_0}\right)$$
$$= x-x_0+\frac{y-y_0}{x}-\frac{y_0}{x_0}+\frac{y_0}{x}$$
$$= x-x_0+\left(\frac{y}{x}-\frac{y_0}{x_0}\right)$$

By differentiation one immediately shows that this is the correct primitive function for Equation (1.62).

2 The Laws of Thermodynamics

The first law

In the last section we realized that heat is nothing but a special form of energy. This was the discovery of R.J. Mayer (1842). The perception of heat as energy which is statistically distributed among the particles of a system, was established by Clausius (1857): he introduced the statistical concept of the mean square of the velocity and derived the ideal gas law from kinetic theory.

In physics, the principle of conservation of energy is of fundamental importance, and experience asserts the assumption that this principle is correct in macroscopic as well as in microscopic dimensions. Therefore, besides the work which is performed by or on a system one has also to consider the heat exchanged with the surroundings. Thus we can assign an *internal energy* U to each macroscopic system. For an isolated system which does not exchange work or heat with its surroundings, the internal energy U is identical to the total energy E of the system known from mechanics or electrodynamics. However, if the system is able to exchange work or heat with its surroundings, an energy law holds which is extended with respect to mechanics or electrodynamics. The change of the internal energy for an arbitrary (reversible or irreversible) change of state is given by the sum of the work δW and heat δQ exchanged with the surroundings. We write

$$\textit{First law:} \qquad dU = \delta W + \delta Q \tag{2.1}$$

Here it is of crucial importance that the work and heat exchanged with the surroundings in a small change of state may depend on the way in which the procedure takes place; i.e., they may not be exact differentials. Therefore we write δ for the changes to distinguish them from exact differentials.

On the other hand, the change of the total energy is independent of the way the procedure takes place and depends only on the initial and final state of the system. The internal energy therefore possesses an exact differential. Once again we explicitly remark that, e.g., the work has the form $\delta W_{\text{rev}} = -p\,dV$ only for reversible processes; for irreversible processes it may be that $\delta W_{\text{irr}} = 0$. The same holds for the exchanged heat: $\delta Q_{\text{rev}} = C_V\,dT$ is only valid for reversible processes, while Equation (2.1) is always true.

There exist many formulations for the first law of thermodynamics, which all have the same meaning, namely that in the energy balance of a system the exchanged work and heat together yield the total change of energy of the system. This perception is mainly due to R. Mayer (1814–1878) and J.P. Joule (1818–1889), who was able to prove with his precise experiments that heat is a special form of energy.

Here we want to present at least a selection of these formulations of the first law, which are all equivalent:

a. The internal energy U of a system is a state function. This means that the total energy content of a system is always the same for a given macroscopic state.

b. There is no perpetuum mobile of the first kind. A perpetuum mobile of the first kind is an engine which permanently generates energy, but does not change its surroundings. It is for instance not only an engine which permanently works without rest, which would, in good approximation, also be true for our planetary system, but it is an engine which effectively performs work without a source of energy.

c. The change of the internal energy for an arbitrary infinitesimal change of state is a total differential.

The equivalence of assertions a) and c) follows from the preceding section: If dU is a total differential, there exists a state function U and vice versa. Assertion b) is also equivalent to c): If b) were not true, there would be a working material for a thermodynamic process where energy would be always generated, although after some time the system reached its initial state; this would contradict the contour-independence of integrating a total differential.

We again stress that the energy law holds independently from the procedure for reversible as well as for irreversible changes of state.

Example 2.1: Internal energy and total differential

As an example we calculate the internal energy of an ideal gas. In the section "kinetic theory of the ideal gas" we have already derived the following equation:

$$pV = NkT = \frac{2}{3} N \langle \epsilon_{\text{kin}} \rangle$$

where $\langle \epsilon_{\text{kin}} \rangle$ was the mean kinetic energy per particle. In the case of the ideal gas the particles possess only kinetic but no potential energy; hence $\langle \epsilon_{\text{kin}} \rangle$ is also the total mean energy. However, the internal energy in the statistical interpretation is nothing but the total mean energy of the system, i.e., with $U = \langle E_{\text{kin}} \rangle = N \langle \epsilon_{\text{kin}} \rangle$

$$U = \frac{3}{2} NkT \tag{2.2}$$

In addition we want to determine the specific heat of the ideal gas. Let us consider a container with an ideal gas at constant volume in a heat bath of temperature T. If the temperature is changed by dT we have

$$dU = \delta W + \delta Q$$

On the other hand, the work exchanged with the surroundings is, because of

$$\delta W = -p\,dV = 0 \qquad V = \text{const.}$$

equal to zero. (Remark: changes of state at constant volume are called *isochoric*). Hence it holds that

$$dU = C_V(T)\,dT \tag{2.3}$$

Here we have used the heat capacity C_V at constant volume. Note that δQ can be integrated for the present procedure. For dilute gases the specific heat is constant (cf. figure in section "Specific heat"), so that we are able to integrate Equation (2.3),

$$U(T) - U_0(T_0) = C_V(T - T_0)$$

If we additionally consider that the *total heat capacity* is proportional to the particle number, $C_V = Nc_V$, we find

$$U(T) - U_0(T_0) = Nc_V(T - T_0) \tag{2.4}$$

where c_V is the constant *specific heat per particle of the ideal gas*. By comparison with Equation (2.2) one obtains

$$c_V = \frac{3}{2}k \qquad \text{or} \qquad C_V = \frac{3}{2}Nk$$

respectively. Again we realize the large practical importance of the specific heat. With the help of Equation (2.3) we can determine the internal energy of real gases from their measured specific heat. Quite generally, we can identify the total heat capacity at constant volume with

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V$$

since Equation (2.3) holds always for $V = \text{const}$. By the way, Equation (2.4) is more general than it seems on first sight: the specific heat of many materials may be assumed to be constant for a certain range of temperatures. Hence Equation (2.4) holds, e.g., also for metals and real gases as long as the considered differences in temperature are not too large.

Example 2.2: Adiabatic equations for the ideal gas

We now ask for the relationship between the temperature and the volume of an ideal gas if there is no heat exchanged with the surroundings. A process in which there is no heat exchange is called an *adiabatic* process. According to the first law, with $\delta Q = 0$ and $\delta W_{\text{rev}} = -p\,dV$ it holds that

$$dU = \delta W_{\text{rev}} = -p\,dV$$

for a reversible adiabatic process. If the system is compressed by the volume dV, i.e., if work is performed on the system, the energy content of the system increases by $dU = -p\,dV > 0$ ($dV < 0$). From equation 2.2 we know that for an ideal gas quite generally (also for $dV \neq 0$) it holds that $dU = C_V dT$. Therefore we obtain a relationship between dT and dV for adiabatic changes of the volume of an ideal gas:

$$C_V\,dT = -p\,dV$$

If we insert the ideal gas law for $p(V, T)$ we obtain

$$C_V\,dT = -\frac{NkT}{V}\,dV \tag{2.5}$$

This is a differential equation which describes the relationship between V and T for adiabatic changes of state. Since $C_V = \text{const.}$ we can integrate Equation (2.5) by separation of variables from an initial state (T_0, V_0) to a final state (T, V),

$$\int_{T_0}^{T} \frac{C_V}{Nk}\frac{dT}{T} = -\int_{V_0}^{V} \frac{dV}{V} \Rightarrow \frac{C_V}{Nk}\ln\frac{T}{T_0} = -\ln\frac{V}{V_0}$$

If we insert $C_V = \frac{3}{2}Nk$ and rearrange terms, we obtain

$$\left(\frac{T}{T_0}\right)^{3/2} = \frac{V_0}{V} \tag{2.6}$$

With the help of the ideal gas law we can derive equivalent equations for the relations between p and V or p and T, respectively; for reversible adiabatic processes, e.g.,

$$\left(\frac{T}{T_0}\right)^{5/2} = \frac{p}{p_0} \quad \text{and} \quad \frac{p}{p_0} = \left(\frac{V_0}{V}\right)^{5/3} \tag{2.7}$$

Equations (2.6) and (2.7) are the adiabatic equations of the ideal gas. Note that they differ logically from the ideal gas law, since here we have considered a specific process (an adiabatic process): exactly as for processes with constant temperature (isotherms), constant pressure (isobars), or constant volume (isochores) we can eliminate a variable of the ideal gas equation. As we will see, for adiabatic, reversible processes the total entropy of the system is constant (they are *isentropes*). Because of $pV^{5/3} = \text{const.}$ the *adiabates* (isentropes) in a pV diagram are steeper than the *isotherms*, for which the law of Boyle and Mariott ($pV = \text{const.}$) holds.

As already mentioned, the first law holds independently of whether a change of state is reversible or irreversible:

$$dU = \delta W_{\text{rev}} + \delta Q_{\text{rev}} = \delta W_{\text{irr}} + \delta Q_{\text{irr}} \tag{2.8}$$

From the example of the isothermal expansion of an ideal gas we have already learned that in general the absolute value of *performed* work is larger for reversible processes than for irreversible processes. Analogously, the *required* work for an irreversible process (compression) is always larger than for the reversible process. Quite generally it holds, taking into account the sign, that

$$\delta W_{\text{irr}} > \delta W_{\text{rev}} = -p\,dV \tag{2.9}$$

In an irreversible process the absolute value of the (negative) waste heat radiated off is always larger than in a reversible process and less heat is needed:

$$\delta Q_{\text{irr}} < \delta Q_{\text{rev}} \tag{2.10}$$

This follows from Equation (2.8), since $\delta W_{\text{irr}} > \delta W_{\text{rev}}$. Example 1.3 illustrates the validity of these relations. In other words, for reversible processes one requires the least work or

produces the most work, respectively, while for irreversible processes a part of the work is always converted into heat which is radiated out of the system (counted with a negative sign). Simultaneously the entropy of the system increases. This increase of entropy, however, cannot be reversed; thus originates the notation "irreversible."

From a practical point of view, cyclic thermodynamic processes are of special interest. They form the basis for all thermodynamic engines, which we will discuss in more detail later on. Some fundamental statements, however, can be made now with the help of the first law. For instance, for a *cycle*, where a working material regains its initial state after a series of changes of state, the equation

$$\oint dU = 0 \tag{2.11}$$

has to be fulfilled, since dU is a total differential and thus contour-independent. If such a cycle nevertheless performs utilizable work, obviously a corresponding amount of heat (extracted from the surroundings) has been converted into this work. We want to study such a cycle with an ideal gas in more detail.

Carnot's process and entropy

This cycle, with an ideal gas as the working material, was presented by Carnot in 1824. Its importance originates from the fact that it is not only to be interpreted as an idealized limiting case of real cycles, but that it will make some principle ideas clear to us. The Carnot process is performed in four successive reversible steps, which we will illustrate in a pV diagram (Figure 2.1):

Step 1. Isothermal expansion from volume V_1 to volume V_2 at constant temperature T_h. For the isotherm it holds that

$$\frac{V_2}{V_1} = \frac{p_1}{p_2} \tag{2.12}$$

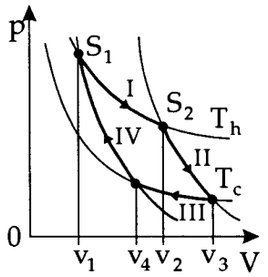

Figure 2.1. Carnot process in the pV diagram.

From Example 2.1 we know that the energy of an ideal gas, which is the working material in our case, cannot be changed at constant temperature. Consequently it holds that

$$\Delta U_1 = \Delta W_1 + \Delta Q_1 = 0 \tag{2.13}$$

From this we can calculate ΔQ_1 with the help of Equation (1.40):

$$\Delta Q_1 = -\Delta W_1 = NkT_h \ln \frac{V_2}{V_1} \tag{2.14}$$

This is the amount of heat exchanged with the heat bath in the first step. Since $V_2 > V_1$, $\Delta Q_1 > 0$; i.e., the amount of heat ΔQ_1 is added to the gas at the expense of the heat bath.

Step 2. Adiabatic expansion of the isolated working material from V_2 to V_3. Here the temperature changes from T_h to T_c. The indices h and c denote *hot* and *cold*, i.e., $T_h > T_c$:

$$\frac{V_3}{V_2} = \left(\frac{T_h}{T_c}\right)^{3/2} \tag{2.15}$$

Since $\Delta Q_2 = 0$ (for adiabatic processes) the work performed in the expansion is taken from the internal energy,

$$\Delta W_2 = \Delta U_2 = C_V(T_c - T_h) \tag{2.16}$$

The sign corresponds to the direction $T_h \to T_c$. For an ideal gas, $C_V = 3Nk/2$; i.e., C_V is a constant independent of temperature and volume. The difference of the internal energies for this part of the process is given by Equation (2.16), although the volume changes, too.

Step 3. We now compress the system isothermally from V_3 to V_4 at the (constant) smaller temperature T_c. Analogously to Step 1 we have

$$\frac{V_4}{V_3} = \frac{p_3}{p_4} \tag{2.17}$$

The work performed during the compression is, because $\Delta U_3 = 0$ at $T = \text{const.}$, submitted to the heat bath in form of heat:

$$\Delta U_3 = \Delta W_3 + \Delta Q_3 = 0 \tag{2.18}$$

$$\Delta Q_3 = -\Delta W_3 = NkT_c \ln \frac{V_4}{V_3} \tag{2.19}$$

This is the amount of heat absorbed by the heat bath in this step. Since $V_4 < V_3$, it follows that $\Delta Q_3 < 0$; i.e., the gas loses this amount of heat.

Step 4. Finally we restore the system to the initial state via an adiabatic compression from V_4 to V_1. The temperature increases again from T_c to T_h:

$$\frac{V_1}{V_4} = \left(\frac{T_c}{T_h}\right)^{3/2} \tag{2.20}$$

Since $\Delta Q_4 = 0$ it follows

$$\Delta W_4 = \Delta U_4 = C_V(T_h - T_c). \tag{2.21}$$

Let us first check the total energy balance of the process. We have

$$\Delta U_{\text{total}} = \underbrace{\Delta Q_1 + \Delta W_1}_{1} + \underbrace{\Delta W_2}_{2} + \underbrace{\Delta Q_3 + \Delta W_3}_{3} + \underbrace{\Delta W_4}_{4} \tag{2.22}$$

If we insert Equations (2.14), (2.16), (2.19), and (2.21), we immediately recognize that indeed $\Delta U_{\text{total}} = 0$, as it should be for a cycle. We have $\Delta Q_1 + \Delta W_1 = 0$ and similarly $\Delta Q_3 + \Delta W_3 = 0$, and furthermore $\Delta W_2 = -\Delta W_4$. In addition, we have the following equations for the amount of heat exchanged with the heat bath:

$$\Delta Q_1 = NkT_h \ln \frac{V_2}{V_1} \qquad \Delta Q_3 = NkT_c \ln \frac{V_4}{V_3} \tag{2.23}$$

On the other hand we have, according to Equations (2.15) and (2.20), that

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \quad \text{or} \quad \frac{V_2}{V_1} = \left(\frac{V_4}{V_3}\right)^{-1} \tag{2.24}$$

Then, however, for ΔQ_1 and ΔQ_3 we have, according to Equation (2.23), that

$$\frac{\Delta Q_1}{T_h} + \frac{\Delta Q_3}{T_c} = 0 \tag{2.25}$$

This equation is of great importance, for it is valid not only for our special Carnot process, but according to all experience, for any *reversible* cyclic process. The quantity $\Delta Q/T$ is also known as *reduced heat.* If we decompose the Carnot process into infinitesimal parts, we may obviously write instead of Equation (2.25)

$$\oint \frac{\delta Q_{\text{rev}}}{T} = 0 \tag{2.26}$$

If we are now able to prove the validity of this equation also for arbitrary closed contours and not only for Carnot's process, then we have shown according to our considerations in the section "Exact and inexact differentials, line integrals" that the reduced heat $\Delta Q_{\text{rev}}/T$ is contour-independent and thus an exact differential. In other words: $1/T$ is the integrating factor of the nonexact differential δQ.

One can deduce the equivalence of Equation (2.26) and the statement that $\delta Q/T$ is an exact differential also from the following consideration: if one integrates from state 1 to state 2 and back again, it follows that

$$\oint \frac{\delta Q}{T} = \int_{C_A} \frac{\delta Q}{T} + \int_{C_B} \frac{\delta Q}{T} = 0 \tag{2.27}$$

If one reverses the direction of integration on the curve C_B (i.e., changes sign), one realizes that the integral $\int_1^2 \delta Q/T$ is contour-independent.

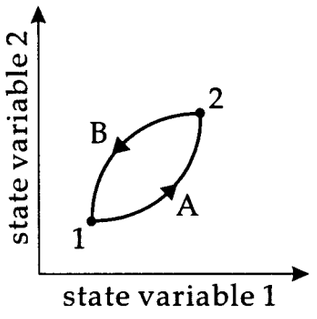

Figure 2.2. Carnot cycle.

To show that Equation (2.26) is contour-independent for an arbitrary cycle (and not only for Carnot's) we divide the arbitrary cycle (Figure 2.2) into a sequence of infinitesimal Carnot-like parts ($N \to \infty$), as illustrated in Figure 2.3. All dashed parts are passed twice by neighboring processes, but for each process in opposite direction, and thus they do not contribute. For sufficiently large N one can always approximate the exact shape of the general cycle by Carnot processes, to any desired accuracy.

Of course, for each of these Carnot processes Equation (2.26) is fulfilled, but therefore also for the sum of all processes and consequently for an arbitrary cycle.

As can be experimentally confirmed, $\delta Q_{\text{rev}}/T$ is an exact differential not only for ideal gases, but for any other reversible thermodynamic process. In other words, there has to exist a *state function*, the total differential of which is $\delta Q/T$. This extensive state function

is the *entropy* S, which is defined via

$$dS = \frac{\delta Q_{\text{rev}}}{T}, \qquad S_1 - S_0 = \int_0^1 \frac{\delta Q_{\text{rev}}}{T} \tag{2.28}$$

Of course, Equation (2.28) can also serve as a measuring instruction. To this end, one has to measure the amount of heat reversibly exchanged by the system at a given temperature T. However, by this method only entropy differences are determined, not absolute values of entropy.

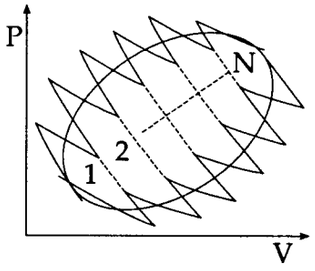

Figure 2.3. Decomposition of an arbitrary cycle into many small Carnot processes.

In the TS plane the Carnot process is just a rectangle: T = const. in steps 1 and 3 and S = const. in steps 2 and 4. The Carnot process effectively performs a work ΔW, as can be seen from the corresponding equations, since the compressional work to be performed in steps 3 and 4 is smaller than the expansion work set free in steps 1 and 2, namely,

$$\begin{aligned} \Delta W &= \Delta W_1 + \Delta W_2 + \Delta W_3 + \Delta W_4 \\ &= -NkT_h \ln \frac{V_2}{V_1} - NkT_c \ln \frac{V_4}{V_3} \end{aligned} \tag{2.29}$$

and using Equation (2.24)

$$\Delta W = -Nk(T_h - T_c) \ln \frac{V_2}{V_1} = -(\Delta Q_1 + \Delta Q_3) \tag{2.30}$$

Since $T_h > T_c$ and $V_2 > V_1$, this is a negative quantity. Hence, ΔW is work performed by the gas. Obviously, a Carnot engine is an engine which transforms heat into work. The work performed by the engine increases with the temperature difference $T_h - T_c$ and with the compression ratio V_2/V_1. We now want to calculate the *efficiency* of this engine. As efficiency we define the ratio between the heat transformed into work and the total heat absorbed,

$$\eta = \frac{|\Delta W|}{\Delta Q_1} = \frac{\Delta Q_1 + \Delta Q_3}{\Delta Q_1} = 1 + \frac{\Delta Q_3}{\Delta Q_1} \tag{2.31}$$

If we insert Equation (2.25), we have

$$\eta = 1 - \frac{T_c}{T_h} = \frac{T_h - T_c}{T_h} \tag{2.32}$$

Thus, the efficiency increases with the temperature difference $T_h - T_c$. However, since one cannot avoid losing a certain amount of heat ΔQ_3, which is radiated off into the cooler heat bath (with T_c), the efficiency (2.32) is appreciably smaller than 1. Therefore, even with this (idealized) engine it is not possible to transform the heat ΔQ_h completely into work, except for the case where the cooler heat bath has the temperature $T_c = 0$ (or the hotter heat bath the temperature $T_h \to \infty$). We will see that there is in principle no heat engine with a better efficiency than Equation (2.32). The impossibility of constructing such an engine leads us to the formulation of the second law of thermodynamics.

Entropy and the second law

The state quantity entropy was introduced by R. Clausius in 1850. It is defined via Equation (2.28) as the amount of heat reversibly exchanged at a temperature T. Since the amount of heat δQ_{irr} exchanged in an irreversible process is always smaller than that exchanged in a reversible process, δQ_{rev}, it holds (sign!) that

$$\delta Q_{\text{irr}} < \delta Q_{\text{rev}} = T\,dS \tag{2.33}$$

Especially for isolated systems, we have $\delta Q_{\text{rev}} = 0$. Therefore, in an isolated system the entropy is constant in thermodynamic equilibrium (reversibility!), and it has an extremum because $dS = 0$. *Every experience confirms that this extremum is a maximum.* All irreversible processes in isolated systems which lead into equilibrium are connected with an increase of entropy, until the entropy assumes its maximum, when equilibrium is reached. This is already a formulation of the second law, which can be abbreviated by a formula:

Second law: For isolated systems in equilibrium it holds that

$$dS = 0, \qquad S = S_{\max} \tag{2.34}$$

and for irreversible processes it holds that

$$dS > 0 \tag{2.35}$$

In irreversible processes the system strives for a new equilibrium state. During this process the entropy of the system grows, until it reaches a maximum in equilibrium. Note that the entropy of a system can also decrease, if the system exchanges heat with its surroundings. For isolated systems, however, $\delta Q = 0$ and in this case Equation (2.34) is correct. The entropy is obviously an *extensive quantity*, since the internal energy as well as the amount of heat are extensive quantities. Therefore, when heat is exchanged at temperature T, the entropy is a quantity analogous to the volume, when compression work is performed against a pressure p. To specify this we once again denote the first law for reversible changes of state in explicit form,

$$dU = \delta Q_{\text{rev}} + \delta W_{\text{rev}} = T\,dS - p\,dV + \mu\,dN + \phi\,dq + \cdots \tag{2.36}$$

Here we have taken into account all possible energy forms that the system may exchange with its surroundings, and we observe that the entropy just fits in the set of extensive state quantities (S, V, N, q, ...) which describe the change of the internal energy under the influence of intensive, locally definable field quantities (T, p, μ, ϕ, ...). In Equation (2.36), the internal energy is a function of the so-called *natural variables* S, V, N, q, ... Here we can also read off the number of state variables which are necessary to uniquely describe a certain state. This is just the number of terms in Equation (2.36), as long as there are no subsidiary conditions to be fulfilled by the state. Such a condition is, for example, the coexistence of various phases. If the function $U(S, V, N, q, \ldots)$ is given, we can determine T, p, μ, ϕ, ... via

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,N,q,\ldots}, \quad -p = \left.\frac{\partial U}{\partial V}\right|_{S,N,q,\ldots}, \quad \mu = \left.\frac{\partial U}{\partial N}\right|_{S,V,q,\ldots}, \quad \ldots \tag{2.37}$$

The function $U(S, V, N, \ldots)$ gives one complete knowledge of the system. Thus, $U = U(S, V, N, \ldots)$ is also called the *fundamental relation.* Equations (2.37) are the corresponding equations of state. *The intensive state quantities are therefore nothing but the derivatives of the fundamental relation with respect to the corresponding extensive state quantities.* On the other hand, if one knows a sufficient number of equations of state, one can determine $U(S, V, N, \ldots)$ up to some integration constants. One may also denote the *entropy* as a function of the other extensive state quantities: $S = S(U, V, N, \ldots)$. The fundamental relation illustrates that the entropy is actually a new notion in thermodynamics. *The state of equilibrium is defined as the state of maximum entropy,* $dS = 0$.

Example 2.3: Entropy of the ideal gas

We want to determine the entropy of an ideal gas at constant particle number as a function of T and V.

For a reversible change of state the first law reads

$$dU = T\,dS - p\,dV \tag{2.38}$$

for $dN = 0$. With the equations of state

$$U = \frac{3}{2}NkT \qquad pV = NkT$$

for an ideal gas we can solve Equation (2.38) for dS:

$$dS = \frac{3}{2}Nk\frac{dT}{T} + Nk\frac{dV}{V}$$

Starting from a state T_0, V_0 with entropy S_0, we integrate this equation,

$$S(T, V) - S_0(T_0, V_0) = \frac{3}{2}Nk\ln\frac{T}{T_0} + Nk\ln\frac{V}{V_0} = Nk\ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\right\} \tag{2.39}$$

and, if we substitute $V \propto T/p$,

$$S(T, p) - S_0(T_0, p_0) = Nk\ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\}$$

Thus, the entropy of an ideal gas increases with temperature and volume. Note, however, that although N appears in Equation (2.39), the equation does not contain the full dependence on N for systems with a variable particle number!

To this end, we should have added the term $\mu\,dN$ in Equation (2.38), and we would have to know the function $\mu(N, V, T)$. Nevertheless, we may conclude the following: since the entropy is an extensive quantity, it has to be proportional to the particle number N, i.e.,

$$S(N, T, p) = Nk\left(s_0(T_0, p_0) + \ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\}\right) \tag{2.40}$$

where $s_0(T_0, p_0)$ is an arbitrary dimensionless function of the reference state (T_0, p_0). In the statistical treatment we will directly calculate values for $s_0(T_0, p_0)$.

Up to now we have considered the entropy from a purely thermodynamic point of view and have assumed some facts known from experience without substantiating them. The meaning of entropy, however, becomes immediately obvious, if we consider its microscopic interpretation.

Insertion: Microscopic interpretation of entropy and of the second law

Statistical considerations are of enormous importance for gaining deeper insight into the purely phenomenological relationships of thermodynamics. As we will see, it is just the second law which establishes a very close connection between the statistical and the phenomenological point of view. The second law formulates the well-known fact that all isolated physical systems converge toward an equilibrium state, where the state quantities do not change anymore after a certain relaxation time. Furthermore, it asserts that this process never reverses itself. A nice example for this fact is a gas which one spontaneously offers a larger volume and which will homogeneously fill this volume after a certain time period. A spontaneous gathering of the gas in one corner of the volume, however, has never been observed, although this would not contradict the law of energy conservation.

The entropy is the state quantity that uniquely characterizes this tendency. Processes which happen spontaneously and lead to equilibrium are connected with an increase in entropy. In equilibrium the entropy thus assumes its maximum value and does not change anymore. Ludwig Boltzmann was the first to show, in his famous *H-theorem* (pronounced Eta-Theorem, H=greek *Eta*) in 1872, that this tendency can also be founded on a statistical description and classical mechanics. In mathematical statistics one can uniquely assign to an arbitrary random event a measure for the predictability of this event. This function is commonly denoted by H and is called uncertainty function (see Chapter 6). Boltzmann was able to show that the uncertainty associated with an arbitrary nonequilibrium velocity distribution can only grow or at least remain equal as a function of time. The Maxwell-Boltzmann velocity distribution (equilibrium distribution) is characterized by a maximum of the uncertainty function. This means that for the Maxwell-Boltzmann distribution the prediction of the momentum of a particle in a gas at given temperature is associated with the largest uncertainty. Analogously, a homogeneous distribution of the particles in coordinate space is associated with the largest uncertainty with respect to the prediction of the coordinates. Other distribution functions (e.g., all particles gathered in a corner of the box) allow for a better prediction. In Chapter 6 the close relationship between the uncertainty function and the entropy is more extensively discussed (both are simply proportional to each other).

An important consequence of the H-theorem is that an arbitrary (nonequilibrium) distribution of particles changes, after a sufficiently long period of time, into the Maxwell-Boltzmann velocity distribution presented in Example 1.2 and that the latter is the only possible equilibrium distribution (cf. also *Quantum Theory: Special Problems*, Exercise 6.5). Many renowned physicists of Boltzmann's day were of the opinion that this seemed to contradict invariance with respect to time reversal, which is a known principle of classical mechanics. This principle guarantees that if one reverses the momenta of all particles in the final state, the process should as well be reversed. In other words, if the diffusion of a gas into a larger volume can be understood in purely mechanical terms, the reverse process, namely the gathering of the gas in a small part of the container, should also be possible, if all momenta of the final state are reversed. This seeming contradiction is resolved by statistical investigation of the problem.

In classical mechanics a state of motion of N particles is uniquely determined by the $3N$ coordinates and $3N$ momenta (q_ν, p_ν) of the N particles at a certain time. The set (q_ν, p_ν) is also called the *microstate* of the system, which of course varies with time. Each microstate (q_ν, p_ν) corresponds to *one* point in a $6N$-dimensional space, the *phase space*. The set (q_ν, p_ν) i.e., the microstate, can therefore be identified with a point in phase space. Let us now consider the diffusion of a gas in an initial state $(q_\nu(t_0), p_\nu(t_0))$ from a smaller into a larger volume. If one is really able to reverse all momenta in the final state $(q_\nu(t_f), p_\nu(t_f))$ and to prepare a state $(q_\nu(t_f), -p_\nu(t_f))$, the process would in fact be reversed. From a statistical point of view, however, this is an event with an incredibly small probability. For there is only one point (microstate) in phase space which leads to an exact reversal of the process, namely $(q_\nu(t_f), -p_\nu(t_f))$. The great majority of microstates belonging to a certain macrostate, however, lead under time reversal to states which cannot be distinguished macroscopically from the final state (i.e., the equilibrium or Maxwell-Boltzmann distribution). The fundamental assumption of statistical mechanics now is that *all* microstates which have the same total energy can be found with equal probability. This, however, means that the microstate $(q_\nu, -p_\nu)$ is only one among very many other microstates which all appear with the same probability.

Let us illustrate this. Although the microstate of the system drastically changes with time also, in macroscopic equilibrium we nevertheless always observe the same macroscopic state quantities such as pressure, temperature, volume, etc. This means that many microstates lead to the same macroscopic state quantities. We will denote by Ω the number of these microstates "compatible" with a given macrostate. However, we can readily convince ourselves that the number of available microstates for a gas which homogeneously occupies a volume V is overwhelmingly larger than the number of available states compatible with a smaller volume. If we characterize the macrostate by the volume V available to our N particles, the number of microstates $\Omega(V)$ available to *one* particle is proportional to V. In fact, a single particle may assume all possible momenta $-\infty < p_\nu < \infty$ and all coordinates q_ν in the volume V. However, the number of coordinate cells is just proportional to the volume V. For N particles which are independent from each other, the numbers of microstates available to each particle have to be multiplied, so that $\Omega(V) \propto V^N$. If we now compare $\Omega(V)$ with the number of microstates in a volume half the size, then $\Omega(V/2)$ is proportional to $(V/2)^N$. Thus, this case is less probable by a factor $(1/2)^N$ than

the case where the gas would homogeneously occupy the whole volume. However, for a macroscopic number of particles, e.g., of the order of Avogadro's number $N_A \approx 10^{23}$, this is an incredibly small number: $(1/2)^{10^{23}}$.

Thus, we can interpret the statement derived from the second law—that the gathering of gas particles in one half of the container is impossible—in statistical terms and assert that it may be possible, but unimaginably improbable. In particular, we thus realize that thermodynamics is a special case of statistical mechanics for very many particles ($N \to \infty$), since then we have $(1/2)^N \to 0$, and the gathering of all particles in one half of the container has zero probability. Note that this holds also for any other arbitrary partial volume of the container, since $q^N \to 0$ for $q < 1$ and $N \to \infty$.

Despite this simple explanation of the seeming contradiction between classical mechanics and the H-theorem, Boltzmann had to fight against sharp criticism of his ideas during his lifetime. Besides the criticism concerning the time reversal invariance of classical mechanics, presented mainly by Loschmidt, there were objections by Zermelo, who emphasized the quasiperiodical behavior of isolated systems (Poincaré cycles).

Objections were raised by Ostwald and Mach, who were pure "thermodynamicists," even against the foundation of Boltzmann's theory, the molecular or atomistic kinetic theory of gases. This last criticism was evidently defeated by Einstein's and Smoluchowski's investigations of brownian motion in 1905.

As we have already realized with the help of a simple consideration, the number of microstates Ω compatible with a given macrostate is a quantity very similar to the entropy of this macrostate. The larger Ω, the more probable is the corresponding macrostate, and *the macrostate with the largest number $\Omega_{\max}$ of possible microscopic realizations corresponds to thermodynamic equilibrium.* Hence, if the particles of a system have arbitrary given coordinates and momenta in the beginning (e.g., a gas which gathers in one corner of a box), (q_ν, p_ν) assume some other values in the course of time, i.e., another possible microstate. All of the many possible microstates correspond to only one macrostate, namely the equilibrium state: thus, after a long period of time, one observes only the equilibrium state, with a probability that is very near to unity. In particular, in this statistical point of view deviations from the equilibrium state are, for a finite number of particles, not impossible (as thermodynamics claims), but only extremely improbable. Especially for very small systems or systems in extreme situations (e.g., gases at the critical point) one may indeed observe deviations from the equilibrium state in the form of *fluctuations* which have, of course, appreciable size only under certain conditions.

We are now able to go one step further and try to establish a connection between the entropy and the number of microstates compatible with a macrostate. For two statistically independent systems the total number of compatible microstates Ω_{tot} is obviously the product of the numbers for the individual systems, namely $\Omega_{\text{tot}} = \Omega_1 \Omega_2$. We have seen that entropy is an extensive state quantity which is simply added for both partial systems: $S_{\text{tot}} = S_1 + S_2$. Furthermore, according to our conclusions after Equation (2.37), the entropy S has to assume a maximum for the equilibrium state, just as the number of compatible microstates Ω assumes a maximum in equilibrium. If we now assume that there is a one-to-one correspondence between entropy and Ω, for instance $S = f(\Omega)$, there is only one mathematical function which simultaneously fulfills $S_{\text{tot}} = S_1 + S_2$ and $\Omega_{\text{tot}} = \Omega_1 \Omega_2$:

the logarithm. Therefore it must hold that $S \propto \ln \Omega$, and this is in fact the fundamental relationship between thermodynamics and statistical mechanics, which we will extensively discuss in the course of this book. In particular, we recognize that the equilibrium state of thermodynamics with a maximum in entropy is the state with the largest number of microscopic possibilities of realizing this state.

With the help of a simple example we can show that even small deviations from the equilibrium state reduce the number Ω of compatible microstates so drastically that they may be observed in nature only as small fluctuations around the equilibrium state.

Example 2.4: Microstates in a simple system

Again we consider a container with volume V, which is homogeneously filled with N particles of a gas in equilibrium. We now imagine the container to be divided into two compartments with volumes V_1 and V_2, where $V_1 + V_2 = V$, and with N_1 and N_2 particles ($N_1 + N_2 = N$), respectively. We set $V_1 = pV$ and $V_2 = qV$. For the fractions p and q of the total volume we of course have $p + q = 1$.

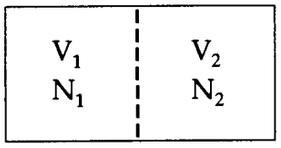

Figure 2.4. Model system.

The total number of microstates compatible with N particles and the total volume V has to be proportional to V^N, as we have already seen. According to the binomial theorem we have

$$\Omega_{\text{tot}}(N, V) \propto V^N = (V_1 + V_2)^N = \sum_{N_1=0}^{N} \binom{N}{N_1} V_1^{N_1} V_2^{N-N_1} \tag{2.41}$$

where $N - N_1 = N_2$. On the other hand,

$$\Omega_1(N_1, V_1) \propto V_1^{N_1}$$

and

$$\Omega_2(N_2, V_2) \propto V_2^{N_2}$$

are just the numbers of microstates compatible with the partial volumes V_1 and V_2 and the particle numbers N_1 and N_2, respectively. Equation (2.41) therefore attains a very illustrative meaning. Let us consider a macrostate with N_1 particles in the partial volume V_1. Obviously there are exactly $\binom{N}{N_1}$ possibilities of selecting these particles from a total of N *enumerated* particles. The number of corresponding microstates is proportional to $V_1^{N_1}$, while for the remaining $N_2 = N - N_1$ particles in the volume V_2 there are still $V_2^{N_2}$ microstates which can be assumed. Each term in the sum is therefore the total number of microstates, if there are N_1 particles in the volume V_1. One now obtains the total number of *all* possible microstates by summing over all possible particle numbers in V_1. Therefore, we may interpret the expression

$$\Omega(V_1, V_2, K, N) = \binom{N}{K} V_1^K V_2^{N-K}$$

as the number of microstates of the situation where K particles are in V_1 and $N - K$ particles in V_2. Then we can furthermore interpret

$$p_K = \frac{\Omega(V_1, V_2, N, K)}{\Omega_{\text{tot}}(V, N)} = \frac{1}{V^N} \binom{N}{K} (pV)^K (qV)^{N-K} = \binom{N}{K} p^K q^{N-K} \tag{2.42}$$

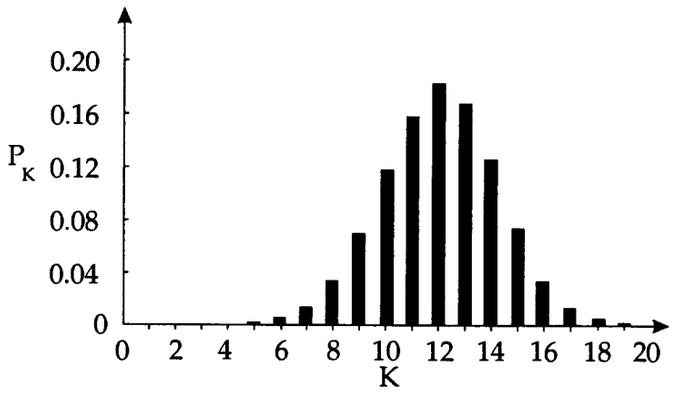

Figure 2.5. Probability of finding K particles in the volume $V_1 = 0.6V$. The total number of particles is $N = 20$.

as the probability that there are just K particles in the fictitious volume V_1 and $N - K$ particles in V_2. With Equation (2.42) we can now immediately find the average particle number in volume V_1. This number is by definition

$$\overline{K} \equiv \sum_{K=0}^{N} p_K K = \sum_{K=0}^{N} \binom{N}{K} K p^K q^{N-K} \tag{2.43}$$

We now apply a trick often used in the calculation of such average values and write Kp^K as $p\frac{\partial}{\partial p}(p^K)$, so that

$$\overline{K} = p\frac{\partial}{\partial p}\sum_{K=0}^{N}\binom{N}{K}p^K q^{N-K} = p\frac{\partial}{\partial p}(p+q)^N = Np(p+q)^{N-1}$$

Since $p + q = 1$ we have $\overline{K} = Np$, or $\overline{K}/N = V_1/V$. On the average, there will be just as many particles in the fictitious volume V_1 as corresponds to the fraction V_1/V. This is of course obvious, since equilibrium corresponds to a homogeneous distribution of particles. Furthermore, we can even calculate the *fluctuations around this value* and ask for the probability of finding a value that deviates from $\overline{K} = Np$. To this end we simply plot the probabilities p_K as a function of K (Figure 2.5). The maximum in the figure just corresponds to the average ($K_{\max} = \overline{K}$).

For our example, with a total of $N = 20$ particles and a volume $V_1 = 0.6V$ it is therefore still quite probable to find 11 or 13 particles in V_1 instead of $\overline{K} = 12$ particles. A definite measure for the size of these deviations from the average value is the mean square deviation. This is defined as

$$\overline{(\Delta K)^2} \equiv \overline{(K - \overline{K})^2} = \sum_{K=0}^{N} p_K (K - \overline{K})^2 = \sum_{K=0}^{N} p_K K^2 - \overline{K}^2 \tag{2.44}$$

since

$$\sum_{K=0}^{N} 2p_K K\overline{K} = 2\overline{K}^2$$

and

$$\sum_{K=0}^{N} p_K = 1$$

The calculation of Equation (2.44) proceeds as in Equation (2.43), but now we have to put

$$K^2 p^K = (p\frac{\partial}{\partial p})^2 p^K$$

and we have

$$\begin{aligned}\overline{(\Delta K)^2} &= (p\frac{\partial}{\partial p})^2 (p+q)^N - (pN)^2 \\ &= p\frac{\partial}{\partial p}(pN(p+q)^{N-1}) - (pN)^2 \\ &= p\Big[N(p+q)^{N-1} \\ &\qquad + pN(N-1)(p+q)^{N-2}\Big] - (pN)^2\end{aligned}$$

If we again insert $p + q = 1$, it follows that

$$\overline{(\Delta K)^2} = pN + p^2N(N-1) - (pN)^2 = pN - p^2N = Np(1-p) = Npq$$

This means that the width of the distribution, measured via

$$\Delta^* K = \sqrt{\overline{(\Delta K)^2}}$$

increases with $\sqrt{N}$. The *relative width*, i.e., the width $\Delta^* K$ with respect to the average particle number in the volume V_1, is then

$$\frac{\Delta^* K}{\overline{K}} = \frac{\sqrt{Npq}}{Np} = \sqrt{\frac{q}{p}}\frac{1}{\sqrt{N}}$$

This represents the fluctuation relative to the (mean) particle number. Here we clearly see that the relative deviation from the equilibrium distribution decreases as $N^{-1/2}$ and is very small for macroscopic particle numbers $N_A \approx 10^{24} \Rightarrow N_A^{-\frac{1}{2}} \approx 10^{-12}$. Hence macroscopic fluctuations (e.g., all particles suddenly in V_1) are extremely improbable. However, small deviations in small spatial regions are quite natural. If we choose a very small partial volume ($p \to 0$), fluctuations can nevertheless be quite large. This corresponds, for example, to local density fluctuations in gases, which are, however, of appreciable size only on a microscopic scale (10^{-8}–10^{-10} m). As already mentioned, these fluctuations can become observable in special situations. For instance, the density fluctuations of a gas in the vicinity of the critical point are especially large. They can be observed by a change in the scattering of light in the gas (critical opalescence). It is very difficult to understand this phenomenon without the help of the statistical point of view.

Now we want to critically review the arguments leading to the important formula $S \propto \ln \Omega$. We will see that two fundamental problems arise, which up to now we implicitly have taken for granted. We started from the example of a gas gathered in a part of the volume of a container, with values $(q_\nu(t_0), p_\nu(t_0))$ for the coordinates and momenta. We then assumed that in the course of time the coordinates and momenta statistically attain some

values and that we therefore find, by counting *all* possible values (Ω), the macrostate with Ω_{max} as the equilibrium state. Exactly at this point, however, we assumed that all microstates (q_ν, p_ν) compatible with our macrostate have "equal rights," i.e., equal probability. In an isolated system the macrostate is characterized by the total energy, the particle number and the volume of the system. We determine Ω by counting all microstates compatible with these values of E, N and V. It may of course be possible that these microstates do not have equal probablities. Let us again consider an example:

Example 2.5: Concerning the equal probability of all microstates

We imagine a box-shaped container and initialize all gas particles at time t_0 in the vicinity of the point P with *parallel* momenta (Figure 2.6). Obviously, this is a microstate which is far from equilibrium. However, if our system behaves ideally, it will *never* reach equilibrium! For if each particle is reflected at the walls in an ideal way, the trajectories will forever stay parallel, and certain regions of coordinate space will never be reached.

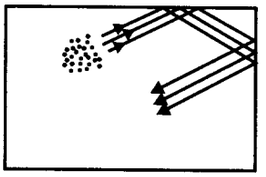

Figure 2.6. Model system.

In addition, the velocities of the particles will change (for pointlike particles without mutual influence) only with respect to the direction, but not with respect to their absolute values. Thus, the Maxwell-Boltzmann distribution will never be reached. This, however, means that we may not assume that all microstates for this system have equal probability. A more detailed consideration shows us that this system is much too idealized. The fundamental objection is that, because of the quantum mechanical uncertainty relation $\Delta x \Delta p > \hbar$, one cannot *in principle* construct such an initial state, so that the particles move randomly in all directions even after a short period of time.

But even in the framework of classical mechanics, where such an initial state is possible, there are actually no ideally reflecting walls and pointparticles without mutual interactions. Even the microscopic structure of a real wall is sufficient to distribute the particles, after a short time, homogeneously over the whole container (not to mention the thermal motion of the particles of the wall and the mutual collisions of the gas particles). Moreover, even the initial conditions $(q_\nu(t_0), p_\nu(t_0))$ can only be determined up to a certain measurement uncertainty, which also leads to diffraction of the beam.

Anyhow, we see that the equal probability of all compatible microstates is an assumption which can only be justified by an experimental examination of the consequences. *Up to now, no one has invented an experiment which disproves this assumption.* We are now likewise able to illustrate another fundamental problem of statistical mechanics with the help of our example. We have stated that a system which is initialized at time t_0 in a nonequilibrium state assumes, with high probability after a certain relaxation time, only microstates $(q_\nu(t), p_\nu(t))$ which belong to the macroscopic equilibrium state, since their number is by far larger than the number of all other microstates. However, here we presuppose that in the course of time the system comes at least very close to each microstate (q_ν, p_ν) *which is compatible with the equilibrium state*. For if certain microstates are never reached (not even approximately),

we actually must not count them in the calculation of Ω! We return to this problem in Part II of this book.

In summary we may therefore say: for every macroscopic thermodynamic state there exists a large number of microscopic realization possibilities. The fact that an isolated system assumes an equilibrium state after a sufficiently long period of time can be traced back to the fact that more microstates belong to the equilibrium state than to a nonequilibrium state. Therefore we may understand the effort of a system to reach a maximum in entropy also as a transition into the most probable state, i.e., into the state with the largest number of microscopic realization possibilities. In particular, the entropy is thus a measure for the number of possible microstates of a system when a macrostate is given.

In a manner similar to the first law we can now formulate also the second law of thermodynamics in different ways.

With respect to the energy law we may for example say:

a) There is no perpetuum mobile of the second kind. A perpetuum mobile of the second kind is an engine which does nothing but perform work while cooling a heat bath. Thus it is an engine which transforms heat into work with 100% efficiency.

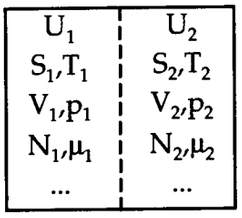

Figure 2.7. The considered system.

From the microscopic point of view the following formulation is especially instructive:

b) Each isolated macroscopic system wants to assume the most probable state, i.e., the state which is characterized by the largest number of microscopic realization possibilities.

Now we want to use both laws to derive some consequences for the state variables T, p, μ, ϕ, ... in an isolated system in equilibrium.

To this end we imagine the completely isolated system to be divided into two parts. Let the total system be characterized by the state variables S, V, and N, where the intrinsic energy U is a function of these variables. *Since the total system is isolated, all these state variables are constant.* There is no exchange of work or heat with the surroundings. Both partial systems, however, can mutually exchange all forms of work or heat.

Therefore the state variables U_i, S_i, V_i and N_i with $i = 1, 2$ do not have constant values; however, it must be the case that

$$U_1 + U_2 = U = \text{const.} \quad S_1 + S_2 = S = \text{const.}$$
$$V_1 + V_2 = V = \text{const.} \quad N_1 + N_2 = N = \text{const.}$$
$$\ldots \tag{2.45}$$

Let us now remember the first law for a reversible change of state for both partial systems:

$$dU_1 = T_1\, dS_1 - p_1\, dV_1 + \mu_1\, dN_1 + \cdots$$
$$dU_2 = T_2\, dS_2 - p_2\, dV_2 + \mu_2\, dN_2 + \cdots \tag{2.46}$$

Here T_i, p_i, and μ_i are the temperatures, pressures and chemical potentials in the two partial systems. Because of Equation (2.45) we now have $dU_1 + dU_2 = 0$. If we therefore add both Equations (2.46), it follows, with $dS_1 = -dS_2, dV_1 = -dV_2, \ldots$, that

$$0 = (T_1 - T_2)\, dS_1 - (p_1 - p_2)\, dV_1 + (\mu_1 - \mu_2)\, dN_1 + \cdots \tag{2.47}$$

Since the change of the variables $S_1, V_1, N_1, \ldots$ in system 1 underlies no restrictions, Equation (2.47) is true only if it separately holds that

$$T_1 = T_2, \quad p_1 = p_2, \quad \mu_1 = \mu_2, \quad \ldots \tag{2.48}$$

These are the necessary conditions for thermodynamic equilibrium. Since the imagined partition of the isolated system was arbitrarily chosen, we can conclude that *if an isolated system is in equilibrium, it has everywhere the same constant temperature, the same pressure and the same chemical potential, etc.* If there is, however, a real wall instead of the fictitious wall separating the partial systems which, for instance, prohibits a change of volume or of the particle number — $dN_1 = 0, dV_1 = 0$ — then only the condition

$$T_1 = T_2 \tag{2.49}$$

remains. Correspondingly, the conditions (2.48) hold also separately or in combination, if the partition is permeable only for certain changes of the state variables. One speaks of thermal, mechanical, chemical, etc., equilibria. If the isolated total system is not in equilibrium, e.g., $T_1 \neq T_2$ and $p_1 \neq p_2$, the relaxation times for reaching equilibrium are in general different for the different variables T, p, μ, ...! It may therefore happen that a system is already to good approximation in thermal equilibrium ($T_1 = T_2$), but not in chemical equilibrium. In most cases, pressure balance occurs most quickly, i.e., mechanical equilibrium is followed by thermal equilibrium. Establishing chemical equilibrium may take very long in some cases. This depends on the speed of the chemical reactions which cause a change dN_i in the particle number.

Global and local equilibrium

If a system is in thermodynamic equilibrium, i.e., if it has everywhere the same temperature, the same pressure and the same chemical potential, one speaks of global equilibrium. However, thermodynamic notions (intensive state quantities) are not restricted to such systems in their applicability. If one can divide the whole system into small partial systems which still contain very many particles and which are individually approximately in thermodynamic equilibrium, these partial systems also can be described by thermodynamic state quantities. However, these quantities will vary from partial system to partial system. The differences in temperature, pressure, and chemical potential affect heat flow (from hotter to cooler parts), volume changes (regions of high pressure expand at the expense of regions with low pressure), and particle fluxes. These fluxes are driven by the corresponding potential differences and cause a compensation of these potentials which leads, for an isolated system, to global equilibrium during the course of time. If the total system can be divided into such parts one speaks of local equilibrium. However, it is of crucial importance that the partial systems can be chosen large enough (having sufficiently many particles) for a statistical description to be reasonable, but on the other hand that in each partial system the (intensive) thermodynamic state quantities assume definite constant values and do not vary too strongly from one partial system to another (small gradients). Then the relationships derived in this book for total systems can be often applied locally in a system which is

actually not in global thermodynamic equilibrium. For instance, in heavy-ion reactions (nucleus–nucleus collisions) drops of nuclear matter collide and different parts of the nuclei have, at a given time, quite different densities, temperatures, particle numbers, etc. Here one can assume partial regions to be approximately in (local) equilibrium. A similar reasoning applies to stars. However, it should be clear that local potential differences and the associated transport phenomena are out of the scope of equilibrium thermodynamics and thus of the present book. They have to be treated with the help of transport theories. Especially the time evolution of a system into (global) equilibrium belongs to this topic.

Thermodynamic engines

Cyclic heat engines play an extraordinarily large role in technics. A large part of the energy used in daily life is produced in such engines, for example in (nuclear) power plants, or combustion engines. The reason is that heat can most easily be produced in various chemical or nuclear processes. The direct generation of utilizable forms of work out of natural sources is, in comparison, far more difficult, e.g., hydroelectric power plants, tidal power plants, wind energy, direct transformation of solar energy into electric energy (galvanic elements, fuel cells). This also confirms the experience that heat as statistically distributed energy is nearly always produced. Now we are able, solely relying on the first and second laws of thermodynamics, to draw far-reaching conclusions concerning the transformation of heat into work. The experience summarized in the second law asserts that the work performed in reversible processes is smallest and the heat largest,

$$\delta W_{\text{irr}} > \delta W_{\text{rev}} = -p\,dV \qquad \delta Q_{\text{irr}} < \delta Q_{\text{rev}} = T\,dS \tag{2.50}$$

For the reversible or irreversible expansion (compression) of an ideal gas we were able to verify the first inequality explicitly. If the ideal gas expands into vacuum without performing work, we have $\delta W_{\text{irr}} = 0$. However, if the gas expands reversibly (always being in equilibrium with an external force), it performs the work $\delta W_{\text{rev}} = -p\,dV$. With $dV > 0$ it thus follows that $\delta W_{\text{irr}} = 0 > \delta W_{\text{rev}} = -p\,dV$. If, on the other hand, the gas is reversibly compressed, we have $\delta W_{\text{rev}} = -p\,dV > 0$. A certain reversible work is required to compress the gas. We have calculated this work in Example 1.3. However, if the gas is irreversibly compressed, for instance, if we suddenly push a piston into a cylinder containing the gas, a part of the work is spent to create turbulence and thus disordered (kinetic) energy, i.e., heat. To compress a gas irreversibly, we thus require more work than in the reversible case. Again it is the case that $\delta W_{\text{irr}} > \delta W_{\text{rev}} = -p\,dV$ ($dV < 0$). Hence, in the irreversible expansion the system performs less work than in the reversible case, and for the irreversible compression one requires more work than in the reversible case.

Quite analogously one understands the second inequality (2.50). For the sake of simplicity we assume that an ideal gas has (in equilibrium) the same temperature after the reversible or the irreversible expansion as it had before. Since the internal energy of an ideal gas depends only on the temperature, it follows that $dU = 0$ and due to the first law that $dU = \delta W + \delta Q = 0$. Therefore, the work performed by the system in the expansion, $\delta W \leq 0$, is taken from the heat bath in the reversible as well as in the irreversible process.

However, for the irreversible expansion $\delta W_{\text{irr}} = 0$ and thus also $\delta Q_{\text{irr}} = 0$. In the reversible expansion the system performs the work $\delta W_{\text{rev}} = -p\,dV < 0$, taken from the heat bath, which provides a constant temperature ($\delta Q_{\text{rev}} = -\delta W_{\text{rev}} > 0$). Hence $\delta Q_{\text{irr}} < \delta Q_{\text{rev}}$. On the other hand, for the isothermal compression it also holds that $\delta W_{\text{irr}} > \delta W_{\text{rev}} > 0$. In the irreversible case the surplus of work (relative to the reversible case) is radiated into the heat bath in the form of a larger (relative to the reversible case) amount of heat, and it holds that $\delta Q_{\text{irr}} < \delta Q_{\text{rev}} < 0$.

If we now have a cyclic engine which leads the working material back to the initial state after one cycle, it holds according to the first law that

$$\oint dU = 0 \tag{2.51}$$

and thus

$$0 = \Delta W_{\text{rev}} + \Delta Q_{\text{rev}} = \Delta W_{\text{irr}} + \Delta Q_{\text{irr}} \tag{2.52}$$

Hence of all possible processes, reversible processes produce the largest amount of utilizable work (because of Equation (2.50), $\Delta W < 0$; this work is performed by the system (given away) and is thus counted as negative) and requires the smallest amount of work ($\Delta W > 0$; this work is performed on the system (added) and is thus counted as positive) for given heat exchange ΔQ. The best efficiency of transforming heat into work is reached by an engine working in a reversible way. As already mentioned, reversible processes are an idealization not present in reality. Such processes would proceed infinitely slowly.

Now we want to calculate the efficiency of a general reversible cyclic process. To this end we schematize the substantial parts of a heat engine in Figure 2.8. Each engine needs a heat reservoir ($T = T_h$) from which to extract heat energy and a second reservoir ($T = T_c$) to absorb the waste heat of the process, i.e., to cool the engine. An engine which works with only *one* reservoir cannot perform utilizable work in a *cyclic process*. According to the first law it holds that

$$0 = \Delta W + \Delta Q_h + \Delta Q_c \tag{2.53}$$

We have already defined the efficiency η as the fraction $|\Delta W|/\Delta Q_h$ (see section about Carnot's process), which tells us how much heat energy ΔQ_h is transformed into work ($\Delta W < 0$, $\Delta Q_h > 0$, $\Delta Q_c < 0$):

$$\eta_{\text{irr}} < \eta_{\text{rev}} = -\frac{\Delta W}{\Delta Q_h} = \frac{\Delta Q_h + \Delta Q_c}{\Delta Q_h} \tag{2.54}$$

Since the engine shall work reversibly, it holds that

$$\delta Q_h = T_h\,dS, \qquad \delta Q_c = -T_c\,dS \tag{2.55}$$

Here dS is the well-defined change in entropy (state function) in a small partial step of the cycle. Note that here $dS \neq 0$, although only equilibrium states occur. The reason is that the engine (working material) is not an isolated system! The signs in Equation (2.55)

correspond to the directions given in the figure. Since $\Delta W < 0$ (performed work) we have

$$\eta = \frac{|\Delta W|}{\Delta Q_h} = \frac{T_h - T_c}{T_h} \tag{2.56}$$

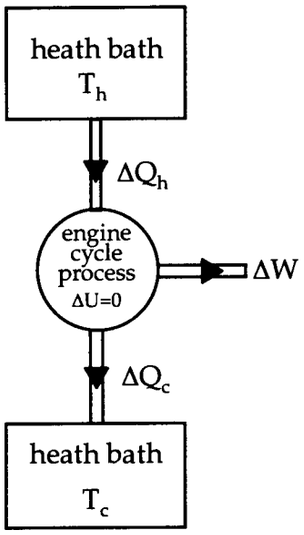

Figure 2.8. Heat engine.

For the efficiency it always holds that $\eta \leq 1$. The transformation of heat into work would only be complete if one could avoid the heat loss (waste heat). This, however, is only possible if the cold reservoir has the temperature $T_c = 0$. On the other hand, from Equation (2.56) it is obvious that not only the temperature of the hot reservoir (e.g., the temperature of the flame of a burner) is important, but also the temperature at which the waste heat is radiated off (the temperature of exhaust gases). To gain a high efficiency the latter temperature should be as small as possible. An important point of our consideration is that Equation (2.56) always holds, independent of the working material and the technical realization of the engine, for if there were two reversible cycles with different efficiencies, one could construct a perpetuum mobile of the second kind.

One would then be able to connect the two processes as shown in Figure 2.9. Engine A works here in the reverse direction, i.e., as a heat pump expelling the energy W_A and the heat Q_{cA} from the cold reservoir as heat Q_{hA} into the hot reservoir. The energy W_A is here generated by the process B, which we shall suppose works with higher efficiency, so that there remains an amount of work $W_B - W_A$. If η_A and η_B denote the efficiencies of the engines (with $\eta_B > \eta_A$), then if we only consider absolute values and choose the signs according to the figure,

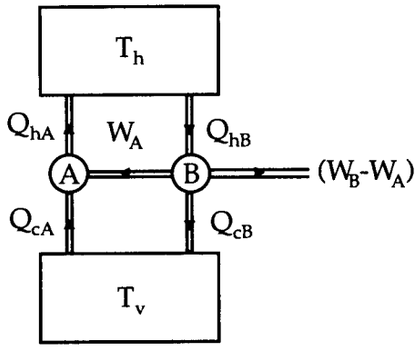

Figure 2.9. Perpetuum mobile of the second kind.

$$\begin{aligned} W_A &= \eta_A Q_{hA} \\ W_B &= \eta_B Q_{hB} \\ Q_{cA} &= Q_{hA} - W_A \\ Q_{cB} &= Q_{hB} - W_B \end{aligned} \tag{2.57}$$

If we now adjust the engine in such a way that $Q_{hA} = Q_{hB} = Q_h$, then there will be no change in the hot reservoir on a long time scale, since the same amount of heat is taken off as pumped back. Then

$$Q_{cA} = (1 - \eta_A)Q_h > Q_{cB} = (1 - \eta_B)Q_h \tag{2.58}$$

since $\eta_B > \eta_A$. Thus the heat

$$\Delta Q_c = Q_{cA} - Q_{cB} = (\eta_B - \eta_A)Q_h \tag{2.59}$$

is effectively drawn off from the cold reservoir. Hence, the engine performs the work

$$W_B - W_A = (\eta_B - \eta_A)Q_h \tag{2.60}$$

while cooling the cold reservoir. This is exactly a perpetuum mobile of the second kind, which permanently performs work and merely cools a heat reservoir. The vain efforts lasting for centuries to construct such an engine, which does not contradict the energy law

but rather the entropy law, resulted in the recognition that $\Delta Q_c = W_B - W_A = 0$, or

$$\eta_A = \eta_B = \frac{T_h - T_c}{T_h} \tag{2.61}$$

for all reversible processes at given T_h and T_c.

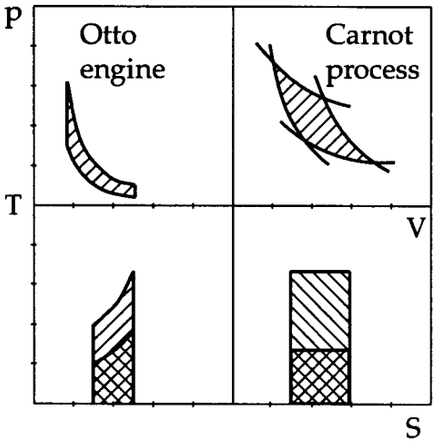

Figure 2.10. Work diagrams of two engines.

Let us now consider the work diagrams of some processes. In the Figure 2.10 the pV diagram and the TS diagram are depicted for the Carnot process. The work performed per cycle corresponds to the hatched area

$$\Delta W = -\oint p\,dV = \oint T\,dS \tag{2.62}$$

It is exactly as large as the difference of the heats $\Delta Q_h = T_h \Delta S$ and $\Delta Q_c = T_c \Delta S$ (see marked areas in the figure). Real processes, as for instance in an Otto-cycle engine, deviate more or less from this diagram. The working materials do not behave ideally and the processes are in most cases strongly irreversible. In addition, in such engines the working material is exchanged after one cycle. Because of irreversibility thermodynamic equilibrium is not achieved in real engines, but the processes are connected with strong turbulence and pressure gradients (especially in the combustion stage), so that the diagrams describe only average properties (average temperature, pressure, etc.).

When interpreting the diagrams of the Otto-cycle engine one should note that two piston cycles correspond to one working cycle (upper dead center, intake stroke, lower dead center, compression, upper dead center, ignition, performance of work, lower dead center, emission of exhaust, upper dead center).

Exercise 2.6: Mixture temperatures

Calculate the range of possible final temperatures T_f in equilibrium for a system consisting of two partial systems A and B, if A and B have initial temperatures T_A, T_B and heat capacities C_V^A, C_V^B which are independent of temperature.

To this end, consider the limiting cases of a totally irreversible process ($\delta W = 0$) and a totally reversible process ($\delta W_{\max}$). Calculate the mechanical work that one can maximally extract from this system and the change of entropy of the partial systems in the irreversible case.

Solution

First case: Totally irreversible process $\delta W = 0, \quad dU = \delta Q_A + \delta Q_B = 0$.
A change in the temperature of the partial systems is connected with an exchanged amount of heat via

$$\delta Q_A = C_A\,dT_A$$

$$\delta Q_B = C_B\,dT_B$$

$$\delta Q_A = -\delta Q_B$$

Thus, for the final temperature T_f follows that

$$\int_{T_A}^{T_f} C_A \, dT_A = -\int_{T_B}^{T_f} C_B \, dT_B$$

Since C_A and C_B do not depend on temperature

$$C_A(T_f - T_A) = -C_B(T_f - T_B)$$

or

$$T_f = \frac{C_A T_A + C_B T_B}{C_A + C_B}$$

Here T_f is the "mixture temperature" for an irreversible process, e.g., when fluids of different temperatures are poured together. The entropy changes are

$$\Delta S_A = \int \frac{\delta Q_A}{T} = \int_{T_A}^{T_f} C_A \frac{dT}{T} = C_A \ln \frac{T_f}{T_A}$$

$$\Delta S_B = \int \frac{\delta Q_B}{T} = \int_{T_B}^{T_f} C_B \frac{dT}{T} = C_B \ln \frac{T_f}{T_B}$$

If, for instance, $T_A > T_B$, then $T_f < T_A$ and $\Delta S_A < 0$, and $T_f > T_B$ and $\Delta S_B > 0$, respectively. However,

$$\Delta S_{\text{tot}} = \Delta S_A + \Delta S_B = C_A \ln \frac{T_f}{T_A} + C_B \ln \frac{T_f}{T_B} \geq 0$$

Second case: Reversible process with a heat engine between A and B:
Now it holds that

$$\Delta S = \Delta S_A + \Delta S_B = 0$$

$$dS = \frac{\delta Q_A}{T_A} + \frac{\delta Q_B}{T_B} = 0$$

from which it immediately follows after integration that

$$\int_{T_A}^{T_f} C_A \frac{dT_A}{T_A} + \int_{T_B}^{T_f} C_B \frac{dT_B}{T_B} = 0$$

or

$$C_A \ln \frac{T_f}{T_A} + C_B \ln \frac{T_f}{T_B} = 0 \Rightarrow \left(\frac{T_f}{T_A}\right)^{C_A} \left(\frac{T_f}{T_B}\right)^{C_B} = 1$$

i.e.,

$$T_f = T_A^{\frac{C_A}{C_A+C_B}} T_B^{\frac{C_B}{C_A+C_B}} = \sqrt[C_A+C_B]{T_A^{C_A} T_B^{C_B}}$$

For a reversible process one obtains the geometrical average of T_A and T_B weighted by C_A and C_B; for an irreversible process one obtains the arithmetical average weighted by C_A und C_B. It always holds that $T_f^{\text{rev}} < T_f^{\text{irr}}$. The work performed by the heat engine in the reversible case is $\delta W = \Delta U = C_A(T_f - T_A) + C_B(T_f - T_B)$.

Exercise 2.7: Room radiator

A room shall have a temperature of 21°C when the outdoor temperature is 0°C. Calculate the relation between the costs of heating if the room is heated with

a. electricity (100% efficiency)

b. a heat pump between T_1 and T_2, if a fraction ϵ of the energy is lost in the heat pump.

Solution According to the scheme, Q_1 is the heat flux (per unit time) which is extracted from the outside. Together with the power W (work per unit time) a heat pump is thus able to supply the room with the heat flux Q_2 (per unit time).

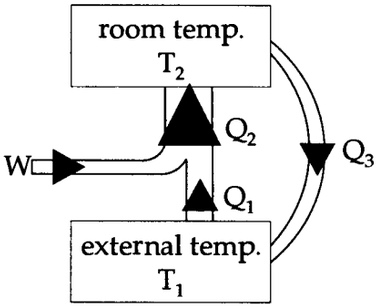

Figure 2.11. Energy fluxes for a heat pump.

The heat flux Q_3 is the emission of heat from the room to the surroundings due to poor isolation. This heat flux Q_3 is proportional to the temperature difference $T_2 - T_1$ ($T_2 > T_1$), i.e.,

$$Q_3 = \gamma(T_2 - T_1)$$

Here the coefficient γ depends on the isolation of the room and is known as *heat emission coefficient.*

Because of the first law, the energy fluxes (with respect to the heat pump) obey

$$W + Q_1 + Q_2 = 0 \tag{2.63}$$

where Q_2 is negative i.e. $|Q_2| = W + Q_1$. The arrows in figure 2.11 indicate the directions of positive energy fluxes. For a reversibly working heat pump

$$\frac{Q_2}{T_2} + \frac{Q_1}{T_1} = 0 \qquad \text{or} \qquad Q_1 = -Q_2 \frac{T_1}{T_2}$$

According to Equation (2.63) it thus follows that

$$W + Q_2 \left(1 - \frac{T_1}{T_2}\right) = 0 \tag{2.64}$$

If outdoor and indoor temperatures agree, no work is needed. However, if $T_1 < T_2$ the work W has to be performed according to Equation (2.64). In the stationary case the heat flux Q_2 has to compensate exactly the loss of heat Q_3. Thus, with $Q_2 = -Q_3$ we have

$$\begin{aligned} W &= -Q_2 \left(1 - \frac{T_1}{T_2}\right) = Q_3 \left(1 - \frac{T_1}{T_2}\right) \\ &= \gamma(T_1 - T_2) \left(1 - \frac{T_1}{T_2}\right) \end{aligned}$$

If we consider that losses occur also in the heat pump, the power W_{eff} supplied to the pump has to be larger by exactly these losses, so that

$$W = W_{\text{eff}}(1 - \epsilon) = \gamma(T_1 - T_2) \left(1 - \frac{T_1}{T_2}\right)$$

For heating with a heat pump we therefore need the work per unit time (power)

$$W_{\text{eff}}^{hp} = \gamma \frac{T_1 - T_2}{1 - \epsilon} \left(1 - \frac{T_1}{T_2}\right)$$

When heating with electricity directly, the power has to compensate the dissipated heat Q_3; therefore it holds that

$$W^{el} = \gamma(T_1 - T_2)$$

The relation between the powers is just

$$\frac{W_{\text{eff}}^{hp}}{W^{el}} = \frac{1}{1 - \epsilon} \left(1 - \frac{T_1}{T_2}\right) \tag{2.65}$$

One observes that heating with a heat pump is for small temperature differences more profitable than heating with electricity. However, the relation (2.65) is not very meaningful, since the heat flux Q_3 also becomes very small for small temperature differences, so that Equation (2.65) does not actually yield the saved energy. To this end, the difference

$$W^{el} - W_{\text{eff}}^{hp} = \gamma(T_1 - T_2)\left(1 - \frac{1}{1 - \epsilon}\left(1 - \frac{T_1}{T_2}\right)\right)$$

is more suitable. As one observes, in the stationary case for an adiabatic room with $\gamma = 0$ it does not matter how one heats, since one does not need any more heating once a temperature is reached.

For the temperatures assumed above

$$\left(1 - \frac{T_1}{T_2}\right) \approx 0.07$$

A heat pump with $\epsilon = 93\%$ loss is therefore, in the stationary case, just as efficient as heating with electricity.

Euler's equation and the Gibbs-Duhem relation

We start from the first law for reversible changes of states for a system which is as general as possible. We assume that the system contains K particle species (chemical components), each of which has, of course, a separate particle number and chemical potential. Then we have

$$dU = T\,dS - p\,dV + \sum_{i=1}^{K} \mu_i\,dN_i \tag{2.66}$$

If in addition further forms of work can be exchanged, for instance, electric or magnetic work, other terms have to be added which have, however, quite analogous forms. Thus, the extensive internal energy U has to be interpreted as a function of the extensive state variables S, V, $N_1, \ldots, N_K$. Now in general, an extensive state variable is proportional to the absolute size of the system. In other words, if one doubles all extensive state variables,

all other extensive quantities also become twice as large. Especially for the internal energy this means that

$$U(\alpha S, \alpha V, \alpha N_1, \ldots, \alpha N_K) = \alpha U(S, V, N_1, \ldots, N_K) \tag{2.67}$$

if α is the enlargement factor. One calls functions which have this property *homogeneous functions of first order*. All extensive variables are homogeneous functions of first order of the other extensive variables. On the other hand, the intensive variables are homogeneous functions of *zeroth* order of the extensive variables,

$$T(\alpha S, \alpha V, \alpha N_1, \ldots, \alpha N_k) = T(S, V, N_1, \ldots, N_k) \tag{2.68}$$

i.e., they do *not* change if we divide or duplicate the system.

Equation (2.67) has far-reaching consequences. For if we consider an infinitesimal increase of the system ($\alpha = 1 + \epsilon$ with $\epsilon \ll 1$), we can expand the left-hand side in a Taylor series:

$$U((1+\epsilon)S, \ldots) = U + \frac{\partial U}{\partial S}\epsilon S + \frac{\partial U}{\partial V}\epsilon V + \cdots + \frac{\partial U}{\partial N_K}\epsilon N_K \tag{2.69}$$

If we insert this into Equation (2.67) and consider that according to Equation (2.66)

$$\frac{\partial U}{\partial S} = T, \quad \frac{\partial U}{\partial V} = -p, \quad \frac{\partial U}{\partial N_1} = \mu_1, \quad \ldots, \quad \frac{\partial U}{\partial N_K} = \mu_K \tag{2.70}$$

it follows that

$$U((1+\epsilon)S, \ldots) = U + \epsilon U = U + \epsilon\left(TS - pV + \sum_i \mu_i N_i\right) \tag{2.71}$$

i.e., *Euler's equation* is valid,

$$U = TS - pV + \sum_i \mu_i N_i \tag{2.72}$$

In other words, from Equation (2.67) it follows that Equation (2.66) may be trivially integrated. This is by no means obvious since according to Equation (2.70) T, p and μ_i are functions of S, V and N_i. If we calculate the total differential of Euler's equation, it holds that

$$dU = T\,dS - p\,dV + \sum_i \mu_i\,dN_i + S\,dT - V\,dp + \sum_i N_i\,d\mu_i \tag{2.73}$$

If we compare this with Equation (2.66), obviously the condition

$$0 = S\,dT - V\,dp + \sum_i N_i\,d\mu_i \tag{2.74}$$

must always be fulfilled (plus additional terms, if other state variables are necessary). One calls Equation (2.74) the *Gibbs-Duhem relation*. It means that the intensive variables $T, p, \mu_1, \ldots, \mu_K$ which are conjugate to the extensive variables $S, V, N_1, \ldots, N_K$ are not all independent of each other. In principle this can be readily understood, since from three extensive state variables, e.g., S, V and N, one can derive only two independent

intensive state variables, e.g., S/N and V/N. All other combinations can be expressed by these. In Equation (2.74) of course S, V, $N_1, \ldots, N_K$ are now functions of the variables T, p, $\mu_1, \ldots, \mu_K$, and this equation provides the possibility to eliminate one of these variables.

Example 2.8: Chemical potential of the ideal gas

Let us demonstrate this with the help of an example: we show that with the help of the Gibbs-Duhem relation (2.74) one can calculate the chemical potential of an ideal gas as a function of T and p. For only one particle species the Gibbs-Duhem relation has the form

$$0 = S\,dT - V\,dp + N\,d\mu$$

or

$$d\mu(p, T) = -\frac{S(p, T)}{N}\,dT + \frac{V(p, T)}{N}\,dp$$

If we here replace $S(T, p)$ by Equation (2.40), we find with the help of $V(T, p) = NkT/p$

$$d\mu(p, T) = -\left(s_0 k + k \ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\}\right)dT + kT\frac{dp}{p} \tag{2.75}$$

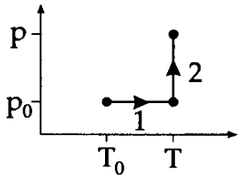

Figure 2.12. Contour of integration.

Since μ is a state quantity and has thus a complete differential (one readily checks the necessary and sufficient condition (1.50)), we may integrate Equation (2.75) along an arbitrary contour from (T_0, p_0) to (T, p). We choose a contour as shown in Figure 2.12.

Then we have

$$\mu(p, T) - \mu_0(p_0, T_0) = -\int_{T_0}^{T}\left(s_0 k + \frac{5}{2}k \ln\left(\frac{T}{T_0}\right)\right)dT + kT\int_{p_0}^{p}\frac{dp}{p} \tag{2.76}$$

where $p = p_0$ and $dp = 0$ on part 1, while $dT = 0$ on part 2. With $\int dx \ln x = x \ln x - x$ we can evaluate Equation (2.76), and find the result

$$\mu(p, T) = \mu(p_0, T_0) - s_0 k(T - T_0) - \frac{5}{2}kT \ln\frac{T}{T_0} + \frac{5}{2}k(T - T_0) + kT \ln\frac{p}{p_0}$$

$$= \mu(p_0, T_0) - kT \ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\} + \left(\frac{5}{2} - s_0\right)k(T - T_0). \tag{2.77}$$

As usual in thermodynamics we only obtain the difference with respect to the initial state (T_0, p_0). The chemical potential depends mainly on the mean kinetic energy of the particles, which is proportional to kT. To add one particle to an ideal gas of temperature T and pressure p in equilibrium, we have to summon the energy $\mu(p, T)$ according to Equation (2.77), no matter how many particles are present before.

Exercise 2.9: Euler's equation for an ideal gas

Show that for an ideal gas Euler's equation

$$U = TS - pV + \mu N \tag{2.78}$$

holds in general, as long as $\mu(p_0, T_0)$ and $s(p_0, T_0)$, the additive, undetermined constants of the chemical potential and the entropy, fulfill a certain relation.

Solution

We first denote our former results for the particular terms. As independent variables we choose N, p and T.

$$U = \frac{3}{2} NkT$$

$$TS = NkTs_0 + NkT \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \right) \right\} \tag{2.79}$$

$$pV = NkT$$

In Equation (2.79) we employed Equation (2.40). With Equation (2.77) it follows that

$$N\mu = N\mu_0 + \left(\frac{5}{2} - s_0 \right) Nk(T - T_0) - NkT \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \right) \right\}$$

Thus Equation (2.78) becomes:

$$\frac{3}{2} NkT = NkTs_0 + NkT \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \right) \right\} - NkT + N\mu_0 + \frac{5}{2} Nk(T - T_0) - s_0 Nk(T - T_0) - NkT \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \right) \right\}.$$

We obtain after appropriate rearrangements

$$\mu_0 \equiv \mu(p_0, T_0) = \left(\frac{5}{2} - s_0 \right) kT_0 \tag{2.80}$$

Since this equation no longer depends on p, T, Euler's equation for an ideal gas is always valid, if relation (2.80) holds for the additive constants. Here (p_0, T_0) of the initial state is completely arbitrary. If one inserts Equation (2.80) into Equation (2.77), we obtain a somewhat more compact notation for the chemical potential of an ideal gas,

$$\mu(p, T) = kT \left[\frac{\mu_0}{kT_0} - \ln \left\{ \left(\frac{T}{T_0} \right)^{\frac{5}{2}} \left(\frac{p_0}{p} \right) \right\} \right]$$

3 Phase Transitions and Chemical Reactions

Gibbs' Phase Rule

We now want to return to the important problem of how many state variables are actually necessary to uniquely determine the state of a system. To this end, we start from an isolated system which contains K different particle species (chemical components) and P different phases (solid, liquid, gaseous, ...). Each phase can be understood as a partial system of the total system and one can formulate the first law for each phase, where we denote quantities of the i^{th} phase by superscript $i = 1, \ldots, P$. For reversible changes of state we have

$$dU^{(i)} = T^{(i)}\, dS^{(i)} - p^{(i)}\, dV^{(i)} + \sum_{l=1}^{K} \mu_l^{(i)}\, dN_l^{(i)}, \qquad i = 1, 2, \ldots P \tag{3.1}$$

Other terms also may appear, if electric or magnetic effects play a role. However, since the corresponding terms have a quite analogous form, Equation (3.1) is sufficiently general. In this formulation of the first law, $U^{(i)}$ of phase i is a function of the extensive state variables $S^{(i)}$, $V^{(i)}$, $N_1^{(i)}, \ldots, N_K^{(i)}$; i.e., it depends on $K + 2$ variables (if further terms appear in Equation (3.1), the number of variables is larger). Altogether we therefore have $P(K + 2)$ extensive state variables. If the total system is in thermodynamic equilibrium, we have in addition the following conditions for the intensive state quantities, cf. Equations (2.45–48):

$$\begin{aligned}
T^{(1)} &= T^{(2)} &&= \cdots = T^{(P)} && && \text{Thermal equilibrium} \\
p^{(1)} &= p^{(2)} &&= \cdots = p^{(P)} && && \text{Mechanical equilibrium} \\
\mu_l^{(1)} &= \mu_l^{(2)} &&= \cdots = \mu_l^{(P)} && l = 1, \ldots, K && \text{Chemical equilibrium}
\end{aligned} \tag{3.2}$$

Each line contains $P - 1$ equations, so that Equation (3.2) is a system of $(P - 1)(K + 2)$ equations. Since $T^{(i)}$, $p^{(i)}$, and $\mu_l^{(i)}$ are functions of $S^{(i)}$, $V^{(i)}$, and $N_l^{(i)}$ we can eliminate one variable with each equation. Thus, we only require

$$(K + 2)P - (K + 2)(P - 1) = K + 2 \tag{3.3}$$

extensive variables to determine the equilibrium state of the total system. As we see, this number is *independent of the number of phases*. If we now consider that exactly P

extensive variables (e.g., $V^{(i)}$, $i = 1, \ldots, P$) determine the size of the phases (i.e., the volumes occupied by each), one needs

$$F = K + 2 - P \tag{3.4}$$

intensive variables. Equation (3.4) is named after J.W. Gibbs and is called *Gibbs' phase rule*. It is readily understood with the help of concrete examples. Let us for instance think of a closed pot containing a vapor. With $K = 1$ we need 3 $(= K + 2)$ extensive variables for a complete description of the system, e.g., S, V, and N. One of these (e.g., V), however, determines only the size of the system. The intensive properties are completely described by $F = 1+2-1 = 2$ intensive variables, for instance by the pressure and the temperature. Then also U/V, S/V, N/V, etc. are fixed and by additionally specifying V one can also obtain all extensive quantities.

If both vapor and liquid are in the pot and if they are in equilibrium, we can only specify one intensive variable, $F = 1 + 2 - 2 = 1$, e.g., the temperature. *The vapor pressure assumes automatically its equilibrium value.* All other intensive properties of the phases are also determined. If one wants in addition to describe the extensive properties, one has to specify for instance V^{li} and V^{v}, i.e., one extensive variable for each phase, which determines the size of the phase (of course, one can also take N^{li} and N^{v}, etc.).

Finally, if there are vapor, liquid, and ice in equilibrium in the pot, we have $F = 1+2-3 = 0$. This means that all intensive properties are fixed: pressure and temperature have definite values. Only the size of the phases can be varied by specifying V^{li}, V^{s}, and V^{v}. This point is also called *triple point* of the system. If we have various chemical components (e.g., air and water) or further terms in Equation (3.1), all assertions hold with a correspondingly larger value of K.

If a system consists of various particle species (chemical components), reactions between particles are often possible, which transform one species into another. Then certain reaction equations, as are often used in chemistry, are valid, for example:

$$2H_2 + O_2 \rightleftharpoons 2H_2O \tag{3.5}$$

In general we can write such reaction equations as

$$a_1 A_1 + a_2 A_2 + \cdots \rightleftharpoons b_1 B_1 + b_2 B_2 + \cdots \tag{3.6}$$

where a_1 particles of species A_1 react with a_2 particles of species A_2 to form b_1 particles of species B_1, etc. The numbers a_i and b_i are the *stoichiometric coefficients* from chemistry. Equation (3.6) is a condition for the particle numbers N_{A_1}, N_{A_2}, ... and N_{B_1}, N_{B_2}, ..., since the changes of these numbers are mutually related by the reaction equation. For instance, let dR be an arbitrary number of reactions of the type of equation (3.6). Then it must hold that

$$\begin{aligned} dN_{A_1} &= -a_1\, dR \\ dN_{A_2} &= -a_2\, dR \\ &\vdots \end{aligned} \tag{3.7}$$

$$dN_{B_1} = b_1\, dR$$

$$dN_{B_2} = b_2\, dR$$

$$\vdots$$

The signs are determined by the fact that in each reaction a_1 particles of species A_1 and a_2 particles of species A_2, etc. vanish, while b_1 particles of species B_1 are created. As we already know, the equilibrium condition for an isolated system reads

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{1}{T}\sum_i \mu_i\, dN_i = 0 \tag{3.8}$$

However, if U and V are constant in such a system, we have from Equation (3.8) the condition

$$\sum_i \mu_i\, dN_i = 0 \tag{3.9}$$

If we insert the dN_i from Equation (3.7) into Equation (3.9), we have after dividing by the common factor dR

$$\sum_i a_i \mu_i = \sum_j b_j \mu_j \tag{3.10}$$

This is a constraint for the chemical potentials, which depends on the reaction equation. With every reaction equation we are therefore able to eliminate another intensive variable. If we have, for instance, R reaction equations, we can formulate an *extended Gibbs' phase rule*:

$$F = K + 2 - P - R \tag{3.11}$$

Also, the total number of extensive variables now becomes smaller ($K + 2 - R$). The reason is that for each phase only $K - R$ components have independent particle numbers; the other numbers can be calculated with the help of the reaction equations.

Example 3.1: Clausius–Clapeyron equation

We want to derive a general equation to determine the vapor pressure of a liquid in equilibrium with its vapor.

We have the following equilibrium conditions for two partial systems which can exchange energy, volume, and particles:

$$T_{li} = T_v, \qquad p_{li} = p_v, \qquad \mu_{li} = \mu_v$$

Because of the Gibbs–Duhem relation these conditions are not independent from each other: if the equation of state is known and if we assume T and p to be given, we can calculate μ_{li} and μ_v. The equation

$$\mu_{li}(p, T) = \mu_v(p, T) \tag{3.12}$$

yields a dependence between p and T; i.e., we can calculate the vapor pressure for a given temperature. If we change the temperature by dT in Equation (3.12), the vapor pressure also has to change by a certain amount dp to account for equilibrium. For the corresponding changes $d\mu_{li}$ and $d\mu_v$ it must hold that

$$d\mu_{li}(p, T) = d\mu_v(p, T)$$

This can be expressed with the Gibbs–Duhem relation $S\,dT - V\,dp + N\,d\mu = 0$ in the following way

$$d\mu_{li}(p, T) = -\frac{S_{li}}{N_{li}}dT + \frac{V_{li}}{N_{li}}dp$$

$$d\mu_v(p, T) = -\frac{S_v}{N_v}dT + \frac{V_v}{N_v}dp$$

or with $s_{li} = S_{li}/N_{li}$, $v_{li} = V_{li}/N_{li}$ and analogously for the vapor:

$$dp(v_{li} - v_v) = dT(s_{li} - s_v)$$

$$\frac{dp}{dT} = \frac{s_{li} - s_v}{v_{li} - v_v}$$

This is the *Clausius–Clapeyron equation.* It is a differential equation for the vapor pressure $p(T)$, if the entropy and volume per particle are known as functions of T and p. Now $S_v - S_{li} = \Delta Q_{li\to v}/T$ is the entropy difference between the liquid and vapor phases. At a given evaporation temperature, this entropy difference corresponds to an amount of heat $\Delta Q_{li\to v}$, which has to be added to evaporate *all* particles from the liquid into the vapor phase. This quantity depends at first also on the amount of liquid to be evaporated. However, changing to the corresponding intensive variables and referring to a certain amount of material, e.g., per particle or per mole,

$$s_v - s_{li} = \frac{S_v}{N_v} - \frac{S_{li}}{N_{li}} = \frac{\Delta Q'_{li\to v}}{T}$$

The sign was chosen according to the direction liquid $\to$ vapor. Now $\Delta Q'_{li\to v} = Q_v/N_v - Q_{li}/N_{li}$ is the amount of heat required to evaporate *one* particle. This quantity can again be a function of pressure (vapor pressure) and temperature. However, in many cases and for not too large temperature differences, this evaporation heat may be considered to be constant. Analogously, the intensive variables v_v and v_{li}, the volume per particle in the vapor and liquid phases, respectively, also are in general functions of vapor pressure and temperature. With the *evaporation heat per particle* $\Delta Q'_{li\to v}$ we thus obtain

$$\frac{dp}{dT} = \frac{\Delta Q'_{li\to v}}{T(v_v - v_{li})} \tag{3.13}$$

Since the righthand side can in general be a complicated function of the vapor pressure p and the evaporation temperature T, one has a differential equation of type $dp/dT = f(p, T)$ for the vapor pressure as a function of temperature, $p(T)$.

For an ideal gas the volume attained by N_A particles at room temperature and a pressure of one atmosphere is 22,400 cm^3, while a liquid like H_2O attains only a volume of 18 cm^3 under these conditions; thus in many cases $v_v \gg v_{li}$ and one has

$$\frac{dp}{dT} \simeq \frac{\Delta Q'}{T v_v} \tag{3.14}$$

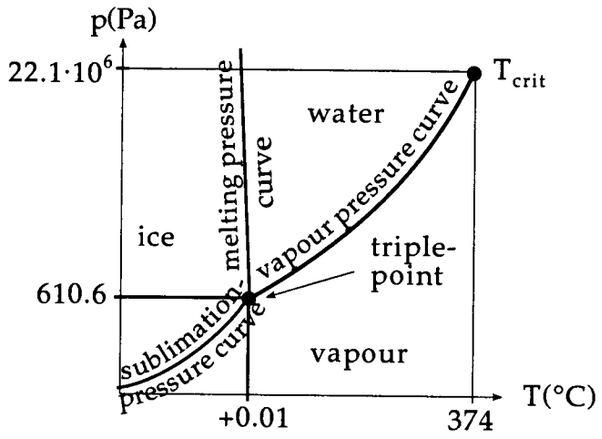

Figure 3.1. Phase diagram of water.

The intensive quantities $\Delta Q'$ and v_v can of course be inserted as measured per mole instead of measured per particle. However, the approximation $v_v \gg v_{li}$ becomes very bad if one approaches the critical point. Then $v_v \simeq v_{li}$ and $\Delta Q'_{li\to v} \simeq 0$. The quotient $\Delta Q'_{li\to v}/(v_v - v_{li})$ nevertheless stays constant (cf. Chapter 17).

Exercise 3.2: Vapor pressure of a liquid

Determine the vapor pressure of a liquid in equilibrium with its vapor under the assumption that the evaporation heat per particle does not depend on pressure or temperature and that the vapor behaves as an ideal gas.

Solution

The best starting point is Equation (3.14):

$$\frac{dp}{dT} = \frac{\Delta Q'}{T v_v}$$

With $v_v = V_v/N_v = kT/p$ we obtain

$$\frac{dp}{dT} = \frac{p}{kT^2}\Delta Q'$$

We may integrate this after separating variables, for instance from an initial temperature T_0 with vapor pressure p_0 to a final temperature T with vapor pressure p,

$$\ln \frac{p}{p_0} = -\frac{\Delta Q'}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

or

$$p(T) = p_0(T_0)\exp\left\{-\frac{\Delta Q'}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right\} \tag{3.15}$$

Thus, the vapor pressure increases strongly with temperature ($\Delta Q' > 0$). Note that Equation (3.15) holds under the same conditions also for the sublimation pressure of a solid: $v_{solid} \ll v_v$ is correct, but the sublimation heat is larger. Thus the pressure curve for sublimation is steeper than the vapor pressure curve. Both curves cross at the triple point.

Now we have understood the essential properties of the phase diagram of a material. Besides the vapor pressure and sublimation pressure curve the melting pressure curve also meets the triple point, since at this point solid, liquid, and vapor phases are simultaneously present. The melting pressure curve, however, has to be calculated from Equation (3.13), since now $v_{solid} \approx v_{li}$. Therefore, the melting pressure curves are very steep in the pT diagram (for $v_{solid} = v_{li}$ they are vertical). For water, the solid phase is less dense than the liquid, $V_{solid} > V_{li}$, but the heat of liquefaction $\Delta Q'_{solid \to li}$ is positive, so that the melting pressure curve falls off very steeply for increasing temperature (negative slope). For most other materials we have $v_{solid} < v_{li}$ and $\Delta Q'_{solid \to li} > 0$; thus the melting pressure curve has a positive slope in these cases. One calls the deviating behavior of water the "water anomaly." For real materials Equation (3.15) is not a very good approximation. Since only intensive variables enter the pT diagram, it says nothing about how much of the material is in one or the other aggregate state.

Phase equilibrium and the Maxwell construction

When we introduced van der Waals' equation of state we already mentioned some inconsistencies of this equation. The isotherms of van der Waals' equation (Figure 3.2),

$$\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = NkT \tag{3.16}$$

show regions of negative pressure as well as mechanically unstable regions having $\partial p / \partial V > 0$, where the gas wants to compress itself. Both cases are certainly unphysical.

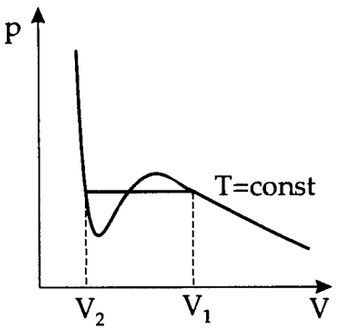

Figure 3.2. Isotherms of the van der Waals gas.

We now want to show that these contradictions can be resolved by considering the phase transition from gas to liquid. Most gases, if we compress them at constant temperature, start to liquefy below a critical temperature at a certain volume V_1.

In equilibrium between vapor and liquid, however, a certain vapor pressure p_v is established, which we have already calculated for an ideal gas from the equilibrium conditions in Exercise 3.2:

$$p_{li} = p_v, \qquad T_{li} = T_v, \qquad \mu_{li}(p, T) = \mu_v(p, T) \tag{3.17}$$

The vapor pressure $p_v(T)$ is solely a function of temperature and does not depend on the vapor volume V, so that one obtains a horizontal isotherm in the pV diagram. An isothermal compression beyond the point of liquefaction V_1 has the effect that more and more vapor is converted into liquid, until at point V_2 the whole amount of gas is liquefied. If we further compress the system the pressure increases strongly because of the small compressibility of the fluid.

It is remarkable that *neither the density of the liquid (given by N/V_2) nor the density of the vapor (given by N/V_1) changes during this phase transition.* The increase of the

average density, which is enforced by the transition from V_1 to V_2, is solely caused by the creation of more and more liquid and the simultaneous reduction of the partial volume of the vapor phase.

The pressure p_s can be calculated from Equation (3.17), if the temperatures and chemical potentials of the vapor and liquid are known. Now, however, we want to present a method known as the *Maxwell construction*: the internal energy $U(V, T)$ at fixed particle number is a state function, which depends only on the volume for a given temperature. For constant temperature we therefore have the energy difference (integrating equation (2.36) for $dN = 0$)

$$\Delta U = T(S_2 - S_1) - \int_{V_1}^{V_2} p(v)\, dV \tag{3.18}$$

between two volumes V_1 and V_2 with the entropies S_1 and S_2 for the purely gaseous and purely liquid phases, respectively. Since U has an exact differential, it cannot matter whether ΔU is calculated along the direct path of constant vapor pressure ($p(V) = p_{fl} = p_v = \text{const.}$) or along the van der Waals isotherm, for which the following holds ($T = \text{const.}$):

$$p(V) = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \tag{3.19}$$

In the first case we simply have ($\Delta Q = T(S_2 - S_1)$ is the latent heat of the phase transition)

$$\Delta U_1 = \Delta Q - p_v(V_2 - V_1) \tag{3.20}$$

and in the case of the van der Waals isotherm we have

$$\Delta U_2 = \Delta Q - NkT \ln \frac{V_2 - Nb}{V_1 - Nb} - N^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \tag{3.21}$$

From the condition

$$\Delta U_1 = \Delta U_2$$

$$\Leftrightarrow -p_v(V_2 - V_1) = -NkT \ln \frac{V_2 - Nb}{V_1 - Nb} - N^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \tag{3.22}$$

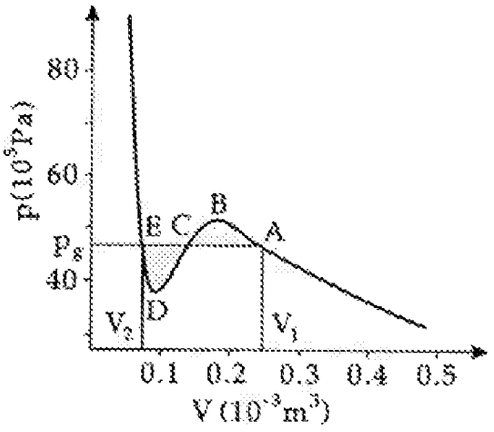

Figure 3.3. Maxwell construction.

one can, in principle, determine the unknown pressure p_v as well as the also unknown volumes V_1 and V_2, if one solves van der Waals' equation for $V_1(p_v, T)$ and $V_2(p_v, T)$. (*Remark:* For a given p_v and T the van der Waals isotherm has also a third (unstable) solution at C, Figure 3.3). However, Equation (3.22) can be understood far more easily. It tells us that the area $p_v(V_2 - V_1)$ of the rectangle between V_1 and V_2 below the unknown vapor pressure equals the area below the van der Waals isotherm.

Or, in other words: the area between the straight line of the vapor pressure and the van der Waals isotherm ABC has to equal the analogous area CDE. (See Figure 3.3.) This is

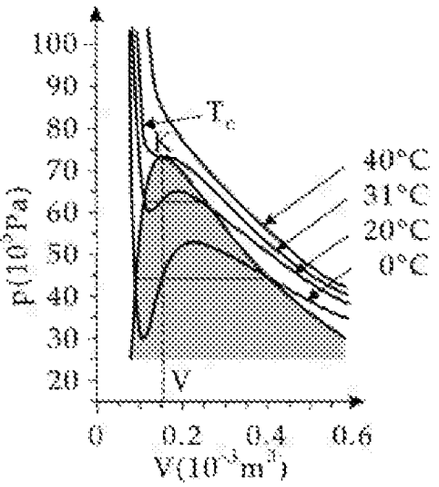

Figure 3.4. Critical point and critical isotherm.

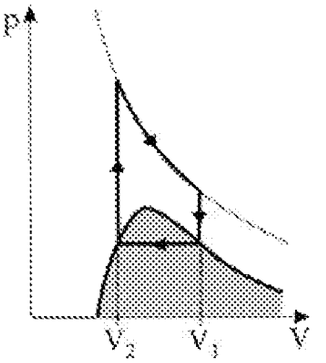

Figure 3.5. Scheme of the considered process.

the well-known *Maxwell construction*. The explicit calculation following Equation (3.22) is equivalent to the Maxwell construction. If one draws the points A and E for a couple of isotherms in a diagram, one obtains the boundary of the phase coexistence region (Figure 3.4). In this region the van der Waals isotherms have to be replaced by straight lines for the vapor pressure. The maximum of the coexistence curve, the so-called *critical point* K, lies on the isotherm, which only has a saddle point (instead of the extrema D and B). Above the critical temperature the Maxwell construction is no longer possible; liquid and gas are no longer distinguishable.

With the help of Figure 3.5 one can also understand another phenomenon. If one isothermally compresses a real gas below the critical temperature until all of the gas is liquefied, then increases the temperature at constant volume V_2 to a point above the critical temperature, and then expands the gas to the initial volume V_1 at constant temperature, one can regain the initial (gaseous) state without a noticeable second phase transition (by a temperature decrease at constant volume).

This means that above the critical temperature (the critical isotherm) a distinction between the gaseous and liquid states is no longer reasonable! This distinction is only possible below the critical temperature, since liquids and gases have very different densities, and thus a *phase boundary surface* exists between the phases. At the critical point, however, the density of the liquid and the gas assume equal values, and a distinction between the phases is no longer possible above the critical temperature.

Because of the importance of the critical point we want to calculate the critical state quantities T_{cr}, p_{cr}, and V_{cr} from van der Waals' equation. The critical point is characterized by the fact that both derivatives vanish (saddle point):

$$\left.\frac{\partial p}{\partial V}\right|_{T_{cr},V_{cr}} = 0, \qquad \left.\frac{\partial^2 p}{\partial V^2}\right|_{T_{cr},V_{cr}} = 0 \tag{3.23}$$

or

$$-\frac{NkT_{cr}}{(V_{cr}-Nb)^2}+\frac{2aN^2}{V_{cr}^3}=0, \qquad 2\frac{NkT_{cr}}{(V_{cr}-Nb)^3}-6\frac{aN^2}{V_{cr}^4}=0 \tag{3.24}$$

If one brings the negative terms to the other sides of the respective equations and divides one equation by the other, one obtains $V_{cr}-Nb=\frac{2}{3}V_{cr}$, and thus

$$V_{cr}=3Nb \tag{3.25}$$

If one inserts this into equation (3.24), one gets

$$T_{cr}=\frac{2aN}{kV_{cr}^3}(V_{cr}-Nb)^2=\frac{2aN}{kV_{cr}^3}\frac{4}{9}V_{cr}^2=\frac{8a}{27kb} \tag{3.26}$$

from V_{cr} and T_{cr} it finally follows with van der Waals' equation that

$$p_{cr}=\frac{Nk8a}{2bN27kb}-\frac{aN^2}{9b^2N^2}=\frac{a}{27b^2} \tag{3.27}$$

The critical state quantities are therefore uniquely determined by the parameters a and b. Hence, for all gases one should have

$$\frac{p_{cr}V_{cr}}{NkT_{cr}}=\frac{a3bN27kb}{27b^2Nk8a}=\frac{3}{8}=0.375 \tag{3.28}$$

Experimentally one finds for Equation (3.28) numbers between 0.25 and 0.35, which once again confirms the qualitative usefulness of van der Waals' equation. On the other hand, a measurement of the critical data of a gas yields a comfortable method for determining the parameters a and b.

By the way, one can also experimentally find the (metastable) parts AB and DE of the van der Waals isotherm in nonequilibrium situations. If a gas is very carefully compressed at constant temperature (avoiding concussions and condensation nuclei), one may follow the isotherm beyond point A nearly up to point B. The same holds for the other side for an isothermal expansion beyond point E to point D. One speaks of *delayed condensation or delayed boiling*, respectively. The system is metastable in this region and switches over to the stable phase coexistence state even under small perturbations. The same phenomena can be observed for isochoric temperature changes. Here one speaks of superheated liquid or supercooled vapor, respectively. Analogous phenomena occur for the solid–liquid phase transition.

The law of mass action

Let us consider a vessel containing a mixture of ideal gases which mutually react, for instance according to Equation (3.6). To take a concrete example, let us take the reaction

$$H_2+Cl_2 \rightleftharpoons 2\,HCl, \qquad \Delta U=-92.3\frac{kJ}{mol(HCl)} \tag{3.29}$$

where an energy of -92.3 kJ/mol is released in an isolated system per mole of hydrochloric acid. At first we have to extend our previous formula for the ideal gas. The purely thermal energy content of an ideal gas of N particles at temperature T was $U = 3NkT/2$. However, this energy does not take into account additional internal energies of different particle species due to their internal structures, different masses, etc. For instance, two molecules, H_2 and Cl_2, differ from two HCl molecules by the chemical binding energy which is released in the reaction. Thus, we have to consider these additional energies in the internal energy and write for each particle species i, with N_i particles at temperature T and pressure p_i:

$$U_i(N_i, T, p_i) = N_i\epsilon_i + \frac{3}{2}N_ikT, \qquad p_iV = N_ikT \tag{3.30}$$

The energies ϵ_i define the different zero points of the energy scales of the respective particles. The difference $2\epsilon_{HCl} - \epsilon_{H_2} - \epsilon_{Cl_2}$, for instance, is the binding energy difference between two molecules of HCl and one molecule of H_2 and Cl_2, respectively. Consequently, the constants ϵ_i appear also in the chemical potentials of the ideal gases (cf. Example 2.8 and Exercise 2.9), since also the energy scales of the chemical potentials are shifted with respect to each other,

$$\mu_i(p_i, T) = \epsilon_i + kT\left(\frac{\mu_{i0}(p_0, T_0)}{kT_0} - \ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p_i}\right)\right\}\right) \tag{3.31}$$

This equation follows as in Exercise 2.9, if one just inserts our new definition for the internal energy. Of course, in the chemical potentials one must insert only the partial pressure of each component, since each component itself fulfills the thermodynamic relations for an ideal gas with N_i particles and pressure p_i at the temperature T common for all particles. Then, the total pressure of the system is $p = \sum_i p_i$ and fulfills $pV = NkT$ with $N = \sum_i N_i$. In particular, the ratio $p_i/p = N_i/N = X_i$ is the molar fraction of the component i and thus a measure for the concentration of particle species i. We can rewrite the equation for $\mu_i(p_i, T)$ using $p_0/p_i = (p_0/p)\cdot(p/p_i) = p_0/(pX_i)$,

$$\begin{aligned}\mu_i(p_i, T) &= \epsilon_i + kT\left(\frac{\mu_i(p_0, T_0)}{kT_0} - \ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\,\frac{1}{X_i}\right)\right\}\right)\\ &= \epsilon_i + kT\left(\frac{\mu_i(p_0, T_0)}{kT_0} - \ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\}\right) + kT\ln X_i\\ &= \mu_i(p, T) + kT\ln X_i\end{aligned} \tag{3.32}$$

This equation means that the chemical potential of component i with the partial pressure p_i in the total pressure p, or with the concentration X_i in the mixture, respectively, can be calculated from the chemical potential of a pure gas of particle species i with total pressure p, if one introduces an additional concentration dependence of the chemical potential. This has the advantage that now all chemical potentials refer to the same total pressure p, and the different partial pressures are taken into account via the concentration X_i. (Note that $\ln X_i = 0$ for $X_i = 1$, pure component i). By the way, this concentration dependence is valid not only for ideal gases, but also for dilute solutions of different components in a

solvent. Such solutions are called *ideal* if the concentration dependence of the chemical potential of particle species i fulfills Equation (3.32). Now we can insert Equation (3.32) into the equilibrium condition, Equation (3.10), and we obtain in general

$$\sum_i a_i \mu_i(p_i, T) = \sum_j b_j \mu_j(p_j, T)$$

$$\sum_i a_i \mu_i(p, T) - \sum_j b_j \mu_j(p, T) = kT \left(\sum_j b_j \ln X_j - \sum_i a_i \ln X_i \right)$$

$$\exp\left\{ \frac{1}{kT} \left(\sum_i a_i \mu_i(p, T) - \sum_j b_j \mu_j(p, T) \right) \right\} = \frac{X_{B_1}^{b_1} X_{B_2}^{b_2} \cdots}{X_{A_1}^{a_1} X_{A_2}^{a_2} \cdots} \tag{3.33}$$

where we have divided by kT in the last step, exponentiated, and exploited the properties of the logarithm. Equation (3.33) is the *law of mass action*, which determines the equilibrium concentrations of products $X_{B_1}, X_{B_2}, \ldots$ and reactants $X_{A_1}, X_{A_2}, \ldots$ in a chemical reaction according to Equation (3.6). One often writes for the lefthand side in Equation (3.33)

$$K(p, T) = \exp\left\{ -\frac{1}{kT} \left(\sum_j b_j \mu_j(p, T) - \sum_i a_i \mu_i(p, T) \right) \right\} \tag{3.34}$$

This is the equilibrium constant of the reaction at the total pressure p and the temperature T. For ideal gases we can readily recalculate this constant for different pressures and temperatures, since we know the chemical potentials $\mu_i(p, T)$ for all pressures and temperatures, if we have determined them once for a standard pressure p_0 and a standard temperature T_0—see Equation (3.31). To this end, we form the ratio of $K(p, T)$ to $K(p_0, T_0)$ and find, with Equation (3.31) that

$$K(p, T) = K(p_0, T_0) \exp\left\{ -\Delta\epsilon \left(\frac{1}{kT} - \frac{1}{kT_0} \right) \right\} \times \left[\left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \right) \right]^{\sum_j b_j - \sum_i a_i} \tag{3.35}$$

with $\Delta\epsilon = \sum_j b_j \epsilon_j - \sum_i a_i \epsilon_i$, the energy gained or required per reaction (the binding energy difference between the products and the reactants). Let us first consider the pressure dependence of the equilibrium constant $K(p, T)$. This depends on whether $\sum_j b_j - \sum_i a_i$ is greater than, less than, or equal to zero. For our example in Equation (3.29), for instance, $a_{H_2} = a_{Cl_2} = 1$ and $b_{HCl} = 2$, i.e., $a_{H_2} + a_{Cl_2} - b_{HCl} = 0$. In the ideal case, such reactions do not show any dependence on the pressure, while for $N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$ we have $\sum_j b_j - \sum_i a_i = -2$. For the latter reaction $K(p, T_0) = K(p_0, T_0)(p/p_0)^2$. Hence, the equilibrium constant increases with increasing pressure. According to Equation (3.33) the concentration of the products has to increase with respect to that of the reactants. The synthesis of ammonia from the elements is therefore more efficient at high pressure than at atmospheric pressure. For this reaction $\Delta\epsilon < 0$ and the equilibrium constant $K(p_0, T) = K(p_0, T_0) \exp\{-\Delta\epsilon(1/kT - 1/kT_0)\}(T_0/T)^5$ decreases with increasing

temperature. To gain a high amount of ammonia one should therefore work at low temperatures. However, in practice the technically very important ammonia synthesis (fertilizer production) is performed at temperatures up to 500°C (and pressures up to 10^8 Pa). This is, from a technical point of view, more convenient than synthesis at room temperature. Our equilibrium considerations namely do not tell us how fast a system assumes equilibrium. In general, the relaxation times needed to reach equilibrium are larger for lower temperatures. At low temperatures the reaction rate is also small. The gain of ammonia per unit time in a continuous reaction, where the reaction products are permanently removed from the system, may therefore be larger at high temperatures, although the equilibrium is actually shifted to disadvantageous values. We do not want to discuss these problems, which belong to the study of reaction dynamics, in more detail. Let us only mention that the reaction rate can be increased by catalytic agents which are not changed by the reaction. Here one exploits the fact that the chemical potential of the materials participating in the reaction is changed if they are absorbed on the surface of certain materials, i.e, if they cling to the surface of the catalyst. Thus, catalytic agents are mainly porous materials with a surface which is as large as possible.

In the following we want to use the concentration dependence of the chemical potential of component i

$$\mu_i(p, T, X_i) = \mu_i(p, T, X_i = 1) + kT \ln X_i \tag{3.36}$$

also for ideal solutions. Here $\mu_i(p, T, X_i)$ is the chemical potential of particle species i in a system at pressure p, temperature T, and with concentration X_i. This can be calculated according to Equation (3.36) from the chemical potential $\mu_i(p, T, 1)$ of the pure component i ($X_i = 1$) at the same p and T. This is a phenomenological equation of state like the ideal gas law and only experience can justify this ansatz. In nonideal solutions Equation (3.36) is not valid. However, one can retain the form of Equation (3.36) also for nonideal systems, if one transforms the term $kT \ln X_i$ to include the activities $kT \ln f_i X_i$, i.e., if one introduces effective concentrations. The f_i are phenomenological parameters which describe the deviations from the ideal case and may depend on the pressure, temperature, and concentration. The form of the law of mass action remains unchanged; one has only to replace the X_i by the effective concentrations $f_i X_i$.

Exercise 3.3: Raoult's law, increase of boiling point

Calculate the dependence of the vapor pressure of a solvent on the concentration of a (not very volatile) dissolved substance and the resulting increase of the boiling point. Consider the vapor and the solution to be ideal.

Solution

As in the calculation of the Clausius–Clapeyron equation we start from the equilibrium condition

$$\mu_v(p, T) = \mu_{li}(p, T, X_{li})$$

where now the chemical potential is changed due to the dissolved substance. It is $X_{li} = N_{li}/(N_{li} + N_{sub})$. The dependence of the chemical potential on the concentration is known

from Equation (3.36):

$$\mu_{li}(p, T, X_{li}) = \mu_{li}(p, T, 1) + kT \ln X_{li} \tag{3.37}$$

where $\mu_{li}(p, T, 1)$ is the chemical potential of the pure solvent. For a given fixed temperature a change of concentration by dX_{li} leads to a change (decrease) of the vapor pressure by dp. Therefore we have the relation

$$\left.\frac{\partial \mu_v(p, T)}{\partial p}\right|_T dp = \left.\frac{\partial \mu_{li}(p, T, 1)}{\partial p}\right|_T dp + kT \frac{dX_{li}}{X_{li}}$$

The Gibbs–Duhem relation,

$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dp$$

however, yields the quite general assertion

$$\left.\frac{\partial \mu}{\partial p}\right|_T = \frac{V}{N} = v$$

and thus we obtain

$$\frac{dp}{dX_{li}} = \frac{kT}{(v_v - v_{li})X_{li}} \tag{3.38}$$

This equation determines the change of the vapor pressure as a function of the concentration of the solvent.

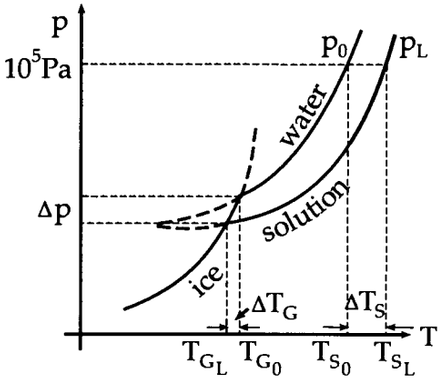

Figure 3.6. Boiling point increase and freezing point decrease.

If we again insert $v_v \gg v_{li}$ and $v_v = V/N_v = kT/p$, we can immediately integrate Equation (3.38). We have

$$\frac{dp}{p} = \frac{dX_{li}}{X_{li}} \Rightarrow \frac{p}{p_0} = \frac{X_{li}}{1}$$

If we have a vapor pressure $p(T, X = 1)$ for a pure solvent at temperature T, the vapor pressure $p(T, X)$ at the same temperature but for the concentration X_{li} is given by

$$p(T, X) = p(T)X_{li} = p(T)(1 - X_{sub})$$

if $p(T)$ is the known vapor pressure for the pure liquid. Here X_{sub} is the concentration of the dissolved substance. The relative decrease of the vapor pressure is therefore, with $p(T) - p(T, X) = \Delta p$, proportional to the molar fraction of the dissolved material:

$$\frac{\Delta p}{p(T)} = X_{sub} \tag{3.39}$$

This is *Raoult's law* (1890). It is, however, not a very good approximation, as one can see from Figure 3.7: even for moderate concentrations of the dissolved material the measured decrease of the vapor pressure deviates from the calculated decrease. One can, however, retain Equation (3.39) if one introduces instead of the true concentration X_{sub} of the substance a reduced, effective concentration $a_{sub} = fX_{sub}$, the so-called activity. The measurement of the vapor pressure then allows for the calculation of the activity coefficient, which is a very important quantity in chemistry.

As one reads off Figure 3.6, for an aqueous solution the boiling pressure of 1 atmosphere is reached only at higher temperatures, due to the decrease in the vapor pressure. This corresponds to an increase in the boiling point. Analogously the triple point (crossing point of the vapor and sublimation pressure curves) is shifted towards lower temperatures, which corresponds to a decrease of the freezing point (at arbitrary pressure).

We can immediately calculate the change in temperature ΔT, if we compare the pressure in the solution with that of the pure solvent:

$$p(T + \Delta T, X_{li}) = p(T, 1)$$

$$(p_0 - \Delta p) \exp\left\{-\frac{\Delta Q'}{k}\left(\frac{1}{T + \Delta T} - \frac{1}{T_0}\right)\right\} = p_0 \exp\left\{-\frac{\Delta Q'}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right\}$$

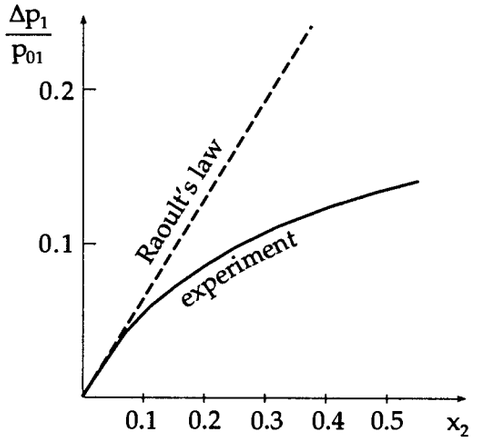

Figure 3.7. Comparison of Raoult's law with experiment.

where Δp is the change of the vapor pressure of the solution compared with the pure solvent at given temperature. Here we have used Equation (3.15). With $1 - \Delta p/p_0 = 1 - X_{sub}$, Equation (3.39), it holds that

$$\ln(1 - X_{sub}) = \frac{\Delta Q'}{k}\left(\frac{1}{T + \Delta T} - \frac{1}{T}\right)$$

For small concentrations $X_{sub} \ll 1$ and for an increase of the boiling point $\Delta T/T$ we have

$$\ln(1 - X_{sub}) \approx -X_{sub}, \qquad \frac{1}{T + \Delta T} \approx \frac{1}{T}\left(1 - \frac{\Delta T}{T}\right)$$

and thus

$$\Delta T \approx \frac{k}{\Delta Q'} T^2 X_{sub} \tag{3.40}$$

Here $\Delta Q'$ is the vaporization latent heat per particle, T is the boiling point of the pure solvent, and X_{sub} is the molar fraction of the dissolved substance.

Equation (3.40) is of great importance for a fast determination of the molecular mass of compounds. If one measures, for known concentration (in kg/m^3) and known vaporization latent heat per particle, the increase of the boiling point, one can determine X_{sub}, and for known N_{li} the particle number N_{sub}, from which one can immediately calculate the mass per particle.

Exercise 3.4: Vapor pressure

Calculate the change of the vapor pressure in a liquid, if a nonsoluble gas is mixed with the vapor.

Solution

The total pressure p of the gaseous phase is constituted by the partial pressures of the vapor, p_v, and of the gas, p_g. The chemical potential depends on the total pressure of the gaseous phase. It is reduced, compared to that of the pure vapor phase, according to

$$\mu_v^{+gas}(p, T) = \mu_v(p, T) + kT \ln \frac{p_v}{p}$$

i.e., the chemical potential is given by that of the pure vapor plus the concentration dependence, in this case expressed by the partial pressure ($X = p_v/p$). The equilibrium condition reads

$$\mu_v^{+gas}(p, T) = \mu_{li}(p, T)$$

If we increase the total pressure at constant temperature by adding a gas, $p = p_v + p_g$, it holds that

$$\left.\frac{\partial \mu_{li}}{\partial p}\right|_T = v_{li}$$

$$\left.\frac{\partial \mu_v}{\partial p}\right|_T = v_v = \frac{V}{N_v} = \frac{kT}{p}$$

$$v_{li}\, dp = \frac{kT}{p}\, dp + kT\, d\left(\ln \frac{p_v}{p}\right)$$

$$= \frac{kT}{p}\, dp + kT\, d(\ln p_v) - kT \frac{dp}{p}$$

$$\frac{d \ln p_v}{dp} = \frac{v_{li}}{kT} \tag{3.41}$$

Equation (3.41) describes the change of the saturation vapor pressure p_v with a change of the total pressure p when adding a gas. If we integrate Equation (3.41) from the situation $p = p_v^{(0)}$ and $p_g = 0$ to the situation $p = p_v + p_g$, we have

$$\ln \frac{p_v}{p_v^{(0)}} = \int_{p=p_v^{(0)}}^{p} dp \frac{v_{li}}{kT} \approx \frac{v_{li}}{kT}\left(p - p_v^{(0)}\right)$$

The integral can be calculated due to the small compressibility of liquids ($v_{li} \approx$ const.). If we insert numbers, e.g., for H_2O at $p = 1.01325 \cdot 10^5$ Pa, $T = 293$K, $v_{li} = 1.8 \cdot 10^{-5}$ m^3/mol, and the vapor pressure without gas $p_v^{(0)} = 607.95$ Pa, we find for a total pressure $p = 1.01325 \cdot 10^5$ Pa with the "gas" air, where one may additionally neglect $p_v^{(0)} \ll p$ and assume $kT/p = v_v \approx 22.4 \cdot 10^{-3}$ m^3/mol, that

$$\ln \frac{p_v}{p_v^{(0)}} \approx \frac{0.018 \cdot 10^{-3}\text{m}^3/\text{mol}}{22.4 \cdot 10^{-3}\text{m}^3/\text{mol}} \approx 8 \cdot 10^{-4}$$

so that the vapor pressure of water is practically independent of the air. One can therefore expand the logarithm around 1 to obtain

$$\ln \frac{p_v}{p_v^{(0)}} = \ln\left(1 + \frac{\Delta p_v}{p_v^{(0)}}\right)$$

$$\approx \frac{\Delta p_v}{p_v^{(0)}} = \frac{v_{li}}{kT}\left(p - p_v^{(0)}\right) \tag{3.42}$$

In practice, however, deviations from this simple formula occur which are caused by the fact that one may not neglect the solubility of the gas in the liquid phase and the interactions of the vapor with the gas. In Figure 3.8 the saturation concentration C_S (instead of the vapor pressure p_v) of steam in different gases is shown. The concentration 200 g/m^3 corresponds to the vapor pressure of pure water without gas. As one observes only H_2 behaves ideally (dashed line). However, one can use Equation (3.42) also for other gases, *if* one inserts instead

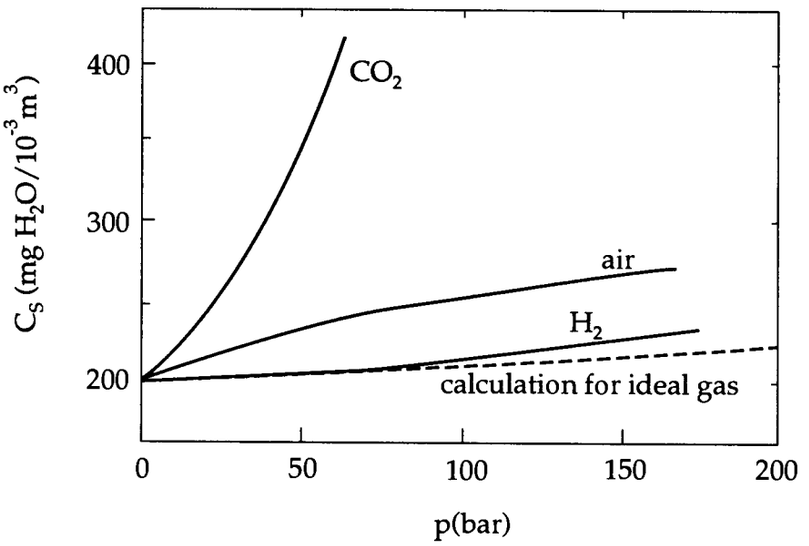

Figure 3.8. Saturation concentrations C_S of different gases in water.

of the pressure an effective pressure (the so-called fugacity), analogously to the activity for concentrations.

Exercise 3.5: The law of Henry and Dalton

Calculate the relation between the pressure of a gas above a nonvolatile solvent and the concentration of the dissolved gas in the solvent.

Solution

If the solvent is nonvolatile, we may neglect its vapor pressure and must postulate in equilibrium

$$\mu_{gas}(p, T) = \mu_{gas}^{dissolved}(p, T, X) \tag{3.43}$$

if X denotes the molar fraction of dissolved gas particles in the solvent. If we insert the concentration dependence of the chemical potential, it follows that

$$\mu_{gas}^{dissolved}(p, T, X) = \mu_{gas}^{dissolved}(p, T, X_0) + kT \ln \frac{X}{X_0}$$

if X_0 is the concentration of a standard solution. If we now vary the gas pressure by dp, the concentration also changes by dX, and with $\partial\mu/\partial p = v$ and Equation (3.43) we have

$$v_{gas}\, dp = v_{gas,X_0}^{dissolved}\, dp + kT\, d \ln \frac{X}{X_0}$$

or

$$\frac{d \ln \frac{X}{X_0}}{dp} = \frac{v_{gas} - v_{gas,X_0}^{dissolved}}{kT}$$

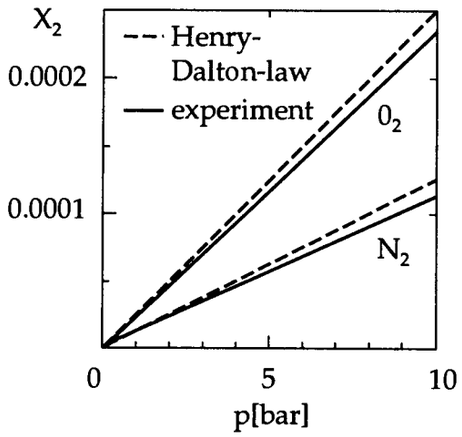

Figure 3.9. Comparison of the law of Henry and Dalton with the experiment.

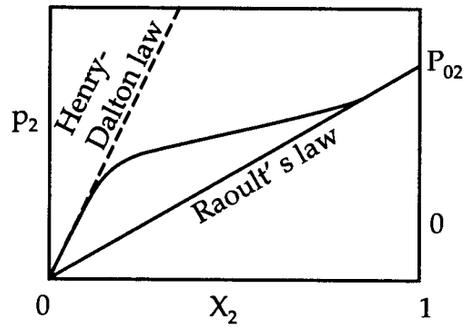

Figure 3.10. Relationship between the law of Henry and Dalton and Raoult's law.

On the righthand side we have the volume difference per gas particle in the gaseous phase and the solution, respectively. With $v_{gas,X_0}^{dissolved} \ll v_{gas} \approx kT/p$ we find after integration

$$\ln \frac{X}{X_0} = \ln \frac{p}{p_0} \quad \text{or} \quad X = X_0 \frac{p}{p_0}$$

This is the *law of Henry and Dalton*, which tells us that the concentration of a gas in a solution increases proportionally to its pressure above the solution. The law holds to good approximation also for the partial pressures of several gases. (See Figure 3.9.)

One can consider the law of Henry and Dalton and Raoult's law of decrease of vapor pressure (Figure 3.10)

$$\frac{\Delta p}{p_0'} = 1 - X$$

or

$$p = X p_0',$$

as limiting cases of one special situation, if one identifies for Raoult's law the nonvolatile solvent with the nonvolatile dissolved material. If X denotes the concentration of the dissolved gas, for small X (low gas pressure) the law of Henry and Dalton is valid; for $X \to 1$, i.e., pure vapor, the pressure is equal to the vapor pressure of the vapor gas p_0'. This, however, holds only for gases which can be liquid at the given temperature. If this is not the case, one can determine a limiting pressure p_0' for $X = 1$ with the help of the Clausius–Clapeyron equation.

Exercise 3.6: Vapor pressure of a mixture

Calculate the vapor pressure of a mixture of two solvents as a function of the molar fraction of solvent 1. Assume that Raoult's law is valid for the partial pressure.

Solution

Raoult's law describing the dependence of the vapor pressure on the concentration of a dissolved material, reads

$$\frac{\Delta p_1}{p_{10}} = X_2 \quad \text{or} \quad \frac{\Delta p_2}{p_{20}} = X_1 \text{ respectively,} \tag{3.44}$$

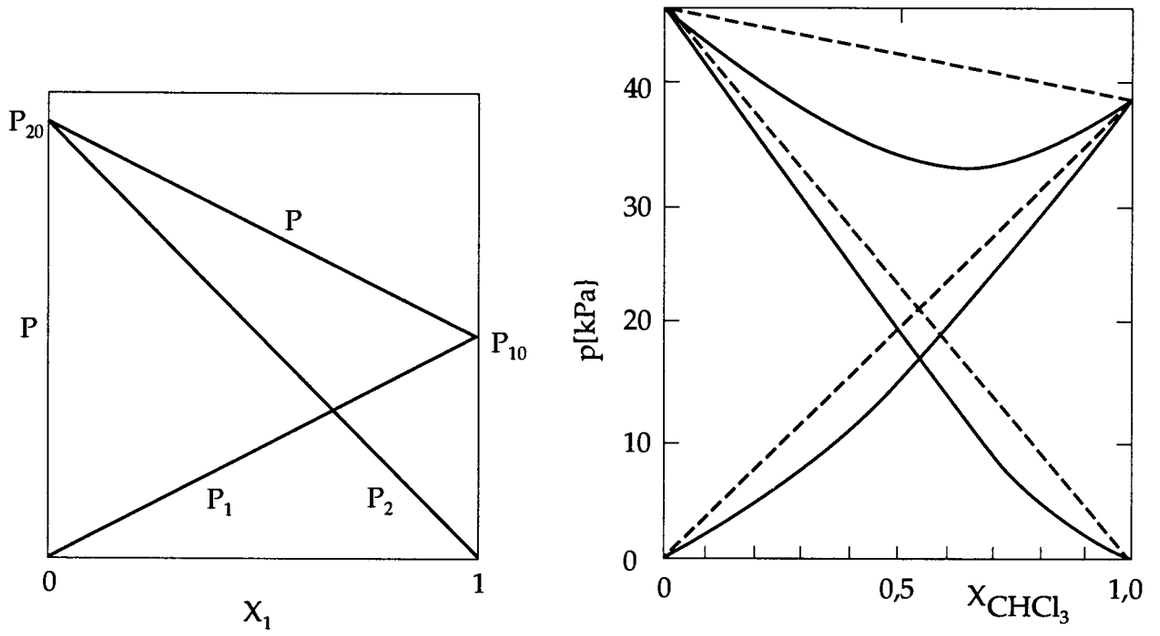

Figure 3.11. Vapor pressure diagram for an ideal mixture and experimental result for chloroform in acetone.

where p_{10} is the vapor pressure of the pure solvent 1 and p_{20} is that of the solvent 2. Note that in deriving Raoult's law we assumed that the dissolved material is nonvolatile, so that we cannot expect a very good agreement with the experiment. We plot Equation (3.44) as a function of X_1. Since $X_2 = 1 - X_1$ we have for the total pressure p

$$p_{10} - p_1 = X_2 p_{10} = (1 - X_1) p_{10}$$

$$p_{20} - p_2 = X_1 p_{20}$$

$$\Rightarrow p_1 + p_2 = p = p_{20} + X_1(p_{10} - p_{20}) \qquad \textbf{(3.45)}$$

As one sees from Figure 3.11, real mixtures differ more or less from the simple theoretical predictions. Here one can also retain Equation (3.45), if one uses fugacities. Conversely, one can determine the fugacities by measuring the partial vapor pressures.

Exercise 3.7: Osmotic pressure

A solvent with a dissolved material is separated from the pure solvent by a diaphragm which is only permeable for the solvent (Figure 3.12). Calculate the pressure difference between the systems as a function of the concentration X_m of the dissolved material. Assume the solution to behave ideally.

Solution

Since the partial systems may exchange energy or particles, it must hold in equilibrium that

$$T_1 = T_2, \qquad \mu_1^{pure} = \mu_2^{solution}$$

However, since the diaphragm is rigid and thus prevents a change of volume, we have in general $p_1 \neq p_2$. We want to calculate this pressure difference. As we know, the chemical potential depends on pressure and concentration, and we have

$$\mu_1^{pure}(p_1, T) = \mu_2^{solution}(p_2, T, X_s) \qquad \textbf{(3.46)}$$

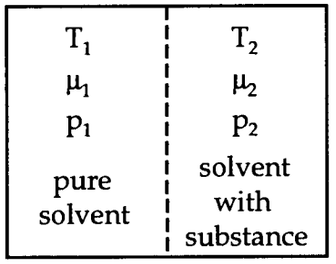

Figure 3.12. The system considered.

for a given concentration X_s of the solvent and X_m of dissolved material, $X_s = 1 - X_m$. With Equation (3.37) we may write

$$\mu_2^{solution}(p_2, T, X_s) = \mu_2^{pure}(p_2, T) + kT \ln X_s \tag{3.47}$$

Here $\mu_2^{pure}(p_2, T)$ denotes the chemical potential of the pure solvent at pressure p_2. Since $\partial\mu/\partial p|_T = v$ we can calculate this chemical potential also for other pressures. It is

$$\mu(p_2, T) = \mu(p_1, T) + \int_{p_1}^{p_2} v(p, T)\, dp$$

If we insert this into Equation (3.47) and the whole expression into Equation (3.46), we obtain

$$\mu_1^{pure}(p_1, T) = \mu_2^{pure}(p_1, T) + \int_{p_1}^{p_2} v(p, T)\, dp + kT \ln X_s$$

Since the compressibility of liquids is small ($v_{li} \approx$ const.) we can evaluate the integral, and find that

$$0 = v(p_2 - p_1) + kT \ln X_s$$

or with $\pi = p_2 - p_1$

$$\pi v = -kT \ln(1 - X_m)$$

For $X_m \ll 1$ we can expand the logarithm and obtain the law of van't Hoff, which resembles the ideal gas law very much,

$$\pi v = X_m kT \tag{3.48}$$

Here π is the osmotic pressure difference, v is the volume per particle in the solvent. The osmotic pressure can attain considerable values. If we, for instance, insert the values for a one molar hydrous solution of salt, the osmotic pressure π is $\approx 24 \cdot 10^5$ Pa.
The importance of Equation (3.48) is due to the fact that one can calculate the molar mass of the dissolved material by determining the easily measurable osmotic pressure, provided the concentration in kg/m^3 and the molar mass of the solvent are known.

Application of the laws of thermodynamics

We want to calculate the internal energy $U(V, T)$ of a real gas. The exact differential of U reads

$$dU = \left.\frac{\partial U}{\partial T}\right|_V dT + \left.\frac{\partial U}{\partial V}\right|_T dV \tag{3.49}$$

We have already identified the expression $\partial U/\partial T|_V = C_V(T, V)$ as the *heat capacity* because of $\delta Q = dU = C_V\, dT$ at $V =$ const. Thus we can determine the temperature

dependence of U at constant volume, provided $C_V(T, V)$ is known. The dependence of the internal energy on the volume shall be expressed by state quantities which are easier to determine. In most cases one has an equation of state $f(T, p, V, N) = 0$, and we want to replace $\partial U/\partial V|_T$ by these quantities (a typical application for thermodynamics), i.e., to express $\partial U/\partial V|_T$ in terms of T and p and derivatives of these intensive variables.

To this end we denote the exact differential of the entropy $S(V, T)$,

$$dS(V, T) = \left.\frac{\partial S}{\partial T}\right|_V dT + \left.\frac{\partial S}{\partial V}\right|_T dV \tag{3.50}$$

for which, on the other hand,

$$dS = \frac{\delta Q_{rev}}{T} = \frac{dU + p\,dV}{T} = \frac{1}{T} C_V\,dT + \left(\frac{1}{T}\left.\frac{\partial U}{\partial V}\right|_T + \frac{p}{T}\right) dV \tag{3.51}$$

also is valid. By comparing coefficients one finds

$$\left.\frac{\partial S}{\partial T}\right|_V = \frac{1}{T} C_V = \frac{1}{T}\left.\frac{\partial U}{\partial T}\right|_V \quad \text{and} \quad \left.\frac{\partial S}{\partial V}\right|_T = \frac{1}{T}\left.\frac{\partial U}{\partial V}\right|_T + \frac{p}{T} \tag{3.52}$$

Since S has an exact differential, it must hold that

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial}{\partial V}\left(\frac{1}{T}\left.\frac{\partial U}{\partial T}\right|_V\right)\Bigg|_T = \frac{\partial^2 S}{\partial T \partial V} = \frac{\partial}{\partial T}\left(\frac{1}{T}\left.\frac{\partial U}{\partial V}\right|_T + \frac{p}{T}\right)\Bigg|_V \tag{3.53}$$

Performing the differentiations yields, with

$$\frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V} \tag{3.54}$$

the result that

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\left.\frac{\partial U}{\partial V}\right|_T + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} - \frac{p}{T^2} + \frac{1}{T}\left.\frac{\partial p}{\partial T}\right|_V \tag{3.55}$$

$$\left.\frac{\partial U}{\partial V}\right|_T = T\left.\frac{\partial p}{\partial T}\right|_V - p \tag{3.56}$$

Thus we have reached our aim to express $\partial U/\partial V|_T$ by derivatives of the equation of state, since we can readily determine $p = p(N, T, V)$ also for real gases. If we insert Equation (3.56) into Equation (3.49) we have

$$dU = C_V(V, T)\,dT + \left(T\left.\frac{\partial p}{\partial T}\right|_V - p\right) dV \tag{3.57}$$

We will see in the next section that such relations are easily derived using the theory of transformations of variables for functions of more than one variable. Here we were forced to explicitly perform all of the individual steps. It is not even necessary to know $C_V(T. V)$, rather it is sufficient to know $C_V(T, V = \text{const.})$. Since dU is an exact differential one has

$$\left.\frac{\partial C_V}{\partial V}\right|_T = \frac{\partial}{\partial T}\left(T\left.\frac{\partial p}{\partial T}\right|_V - p\right)\Bigg|_V \tag{3.58}$$

However, the righthand side can be as well determined from the equation of state, so that we can calculate the volume dependence of the heat capacity. For an ideal gas one has, for instance,

$$p(N, V, T) = \frac{NkT}{V} \tag{3.59}$$

and thus

$$T \left.\frac{\partial p}{\partial T}\right|_V - p = 0 \Rightarrow \left.\frac{\partial C_V}{\partial V}\right|_T = 0 \tag{3.60}$$

Therefore, the heat capacity of an ideal gas cannot depend on the volume. As we already know, it is even absolutely constant.

Exercise 3.8: Internal energy of the van der Waals gas

Calculate the internal energy of a van der Waals gas as a function of temperature and volume at constant particle number.

Solution

The equation of state of the van der Waals gas reads

$$\left(p + \left(\frac{N}{V}\right)^2 a\right)(V - Nb) = NkT$$

We now evaluate the expression $T \left.\frac{\partial p}{\partial T}\right|_V - p$:

$$p(N, V, T) = \frac{NkT}{V - Nb} - \left(\frac{N}{V}\right)^2 a$$

$$\left.\frac{\partial p}{\partial T}\right|_V = \frac{Nk}{V - Nb} \tag{3.61}$$

$$T \left.\frac{\partial p}{\partial T}\right|_V - p = \left(\frac{N}{V}\right)^2 a$$

Hence, as for the ideal gas, the heat capacity of a van der Waals gas cannot depend on the volume because of

$$\left.\frac{\partial C_V(T, V)}{\partial V}\right|_T = \left.\frac{\partial}{\partial T}\left(\frac{N}{V}\right)^2 a\right|_V = 0$$

Thus we have according to Equation (3.57)

$$dU = C_V(T)\, dT + \left(\frac{N}{V}\right)^2 a\, dV$$

We can integrate this starting from an initial state T_0 and p_0 with the internal energy U_0,

$$U(V, T) - U_0(V_0, T_0) = \int_{T_0}^{T} C_V(T)\, dT - N^2 a \left(\frac{1}{V} - \frac{1}{V_0}\right)$$

For temperature differences which are not too large $C_V(T)$ is approximately constant and thus

$$U(V, T) = U_0(V_0, T_0) + C_V(T - T_0) - N^2 a \left(\frac{1}{V} - \frac{1}{V_0} \right) \tag{3.62}$$

The internal energy increases with the volume. This is quite obvious from a microscopic point of view, since the particles are on the average further away from each other, but the interaction is attractive. For large volumes (i.e., small particle densities) Equation (3.62) becomes the result for the ideal gas; i.e., the larger V is, the smaller is the increase of U with V.

Exercise 3.9: Entropy of the van der Waals gas

Calculate the entropy of a van der Waals gas as a function of temperature and volume at constant particle number.

Solution

According to Equations (3.50), (3.51), and (3.56), we have

$$\begin{aligned} dS &= \left.\frac{\partial S}{\partial T}\right|_V dT + \left.\frac{\partial S}{\partial V}\right|_T dV \\ &= \frac{1}{T} C_V(T)\, dT + \frac{1}{T} \left(\left.\frac{\partial U}{\partial V}\right|_T + p \right) dV \\ &= \frac{1}{T} C_V(T)\, dT + \left.\frac{\partial p}{\partial T}\right|_V dV \end{aligned}$$

The quantity $\partial p/\partial T|_V$ for a van der Waals gas was calculated in the preceding Exercise; if we insert Equation (3.61), we obtain

$$dS = \frac{1}{T} C_V(T)\, dT + \frac{Nk}{V - Nb}\, dV$$

Starting from a state T_0 and V_0 with entropy S_0 we can integrate this equation:

$$S(V, T) - S_0(V_0, T_0) = \int_{T_0}^{T} \frac{C_V(T)}{T}\, dT + Nk \ln \frac{V - Nb}{V_0 - Nb}$$

For temperature differences that are not too large ($\approx$ 100K) we have $C_V \approx$ const. and thus

$$S(V, T) = S_0(V_0, T_0) + C_V \ln \frac{T}{T_0} + Nk \ln \frac{V - Nb}{V_0 - Nb}$$

The entropy of a van der Waals gas is nearly identical to that of an ideal gas; one only has to reduce the volume by the proper volume Nb of the particles.

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4 Thermodynamic Potentials

The principle of maximum entropy

The assertion of the second law of thermodynamics is that isolated systems strive for an equilibrium state which is characterized by a maximum in entropy. As we have seen this is, from the microscopic point of view, the most probable state, i.e., the state with the largest number of microscopic realization possibilities.

All spontaneous (irreversible) processes in an isolated system increase the entropy, until the maximum is reached for the equilibrium state:

$$dS = 0, \qquad S = S_{\max} \tag{4.1}$$

On the other hand, we know from mechanics, electrodynamics, and quantum mechanics that systems which are not isolated want to minimize their energy. For instance, mechanical systems want to assume a state with a minimum of potential energy. A raindrop falls onto the earth, where its kinetic energy, gained from its initial potential energy, is transformed into heat. Similar arguments apply to a pendulum which finally reaches its rest position (equilibrium) due to the influence of friction; i.e., it assumes a state with a minimum of potential energy. However, if in both cases one adds the heat energy created, the total energy is not changed. It has merely been statistically distributed in the form of heat among a larger number of particles (earth, support). During this process the entropy of the isolated total system (earth+air+raindrop or pendulum+air+support) has increased. *This leads us to the presumption that the striving for minimum energy can be traced to the striving for maximum entropy*. This can be readily understood with the help of the laws of thermodynamics. To this end, we consider an isolated system containing two partial systems (Figure 4.1). We remove a certain work $\delta W_1 < 0$ from system 1, e.g., a difference in potential energy.

The partial system shall not exchange any heat with the surroundings during this process. For this reversible process we have

$$\delta Q_1 = T\, dS_1 = 0 \tag{4.2}$$

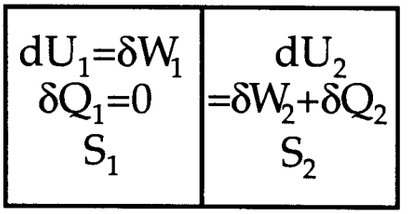


Figure 4.1. Considered system.

hence the entropy S_1 stays constant. If we now hand over a fraction ϵ of the work δW_1 as heat and a fraction $(1-\epsilon)$ as work to partial system 2, we have

$$dU_2 = \delta Q_2 + \delta W_2 = -dU_1 = -\delta W_1 > 0 \tag{4.3}$$

$$\delta Q_2 = -\epsilon\,\delta W_1 > 0, \qquad \delta W_2 = -(1-\epsilon)\,\delta W_1 \tag{4.4}$$

If the heat is passed over to system 2 while the temperature stays constant, the following holds:

$$\delta Q_2 = T\,dS_2 > 0 \tag{4.5}$$

Since now $S_1 = \text{const.}$ and $dS_2 > 0$, the total entropy of the isolated system has obviously increased through the transformation of work from partial system 1 into heat in partial system 2, and the internal energy of partial system 1 has decreased. One furthermore notices that this process proceeds spontaneously as long as partial system 1 can perform work, or in other words, until the total system reaches the state of maximum entropy. The transformation of work into heat is always an irreversible process and happens only until no more work can be performed (pendulum!).

This conclusion can be expressed in very general terms: a nonisolated system at constant entropy ($\delta Q = 0$) heads for a state of minimum energy. Here one has to assume that at least a part of the work δW_1 is transformed into heat. However, if on the contrary $\epsilon = 0$ and $\delta W_1 = -\delta W_2$, then $S_1 = \text{const.}$ and $S_2 = \text{const.}$ (because of $\delta Q_2 = 0$). The process is reversible and cannot happen spontaneously. As was shown, the principle of minimum energy can be derived from the principle of maximum entropy.

Entropy and energy as thermodynamic potentials

In many examples we have already seen that the entropy or the internal energy, respectively, are the central state quantities. If they are known as functions of the natural variables $(U, S, V, N, \ldots)$ of an isolated system, it is guaranteed that also all other thermodynamic quantities are completely known. For example, if we know $U(S, V, N, \ldots)$, it holds that

$$dU = T\,dS - p\,dV + \mu\,dN + \ldots \tag{4.6}$$

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,N,\ldots}, \quad -p = \left.\frac{\partial U}{\partial V}\right|_{S,N,\ldots}, \quad \mu = \left.\frac{\partial U}{\partial N}\right|_{S,V,\ldots}, \quad \ldots \tag{4.7}$$

so that also the temperature, pressure, and chemical potential are known as functions of the natural variables. A similar assertion holds also for the entropy $S(U, V, N, \ldots)$, if we rearrange Equation (4.6):

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN - \ldots \tag{4.8}$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N,\ldots}, \quad \frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N,\ldots}, \quad -\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_{U,V,\ldots}, \quad \ldots \tag{4.9}$$

Equations (4.7) and (4.9), respectively, are the equations of state of the system. On the other hand, knowing all equations of state we may calculate the entropy and the internal energy, respectively, as functions of the natural variables by integration.

Example 4.1: The entropy of the ideal gas

We want to demonstrate this with the help of an example. Let us consider the entropy of the ideal gas, as given in Equation (2.40):

$$S(N, T, p) = Nk\left[s_0(T_0, p_0) + \ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\}\right]$$

If we rewrite this in terms of the independent variables U, N, and V using $U = \frac{3}{2}NkT$ and $pV = NkT$ ($U_0 = \frac{3}{2}N_0kT_0$ and $p_0V_0 = N_0kT_0$, respectively), we obtain

$$S(N, V, U) = Nk\left[s_0(N_0, V_0, U_0) + \ln\left\{\left(\frac{N_0}{N}\right)^{5/2}\left(\frac{U}{U_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\right\}\right] \tag{4.10}$$

Knowing Equation (4.10) all equations of state of the ideal gas can be obtained by partial differentiation according to Equation (4.9),

$$\left.\frac{\partial S}{\partial U}\right|_{N,V} = \frac{1}{T} = \frac{3}{2}Nk\frac{1}{U} \Rightarrow U = \frac{3}{2}NkT \tag{4.11}$$

$$\left.\frac{\partial S}{\partial V}\right|_{N,U} = \frac{p}{T} = Nk\frac{1}{V} \Rightarrow pV = NkT \tag{4.12}$$

$$\left.\frac{\partial S}{\partial N}\right|_{U,V} = -\frac{\mu}{T} = k\left[s_0 + \ln\left\{\left(\frac{N_0}{N}\right)^{5/2}\left(\frac{U}{U_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\right\}\right] - \frac{5}{2}k \tag{4.13}$$

If one inserts Equation (4.11) and (4.12) into (4.13), one gets for the chemical potential

$$\mu(p, T) = kT\left(\frac{5}{2} - s_0\right) - kT\ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\} \tag{4.14}$$

which coincides up to an additive constant with Equation (2.77).
By the way, by comparison we again obtain the relation $\mu_0 = (\frac{5}{2} - s_0)kT_0$. Let us remember that the chemical potential, according to Equation (4.14), yields no independent equation of state, but is related to T and p via the Gibbs–Duhem relation.

However, the knowledge of the state function (fundamental relation) $S(U, N, V, \ldots)$ yields even more information. If the entropy can be enlarged by a change in the variables $U, N, V, \ldots$, the corresponding process happens spontaneously and irreversibly. The equilibrium state of the system is finally given by a maximum of the entropy as a function of the

variables (U, N, V, ...). Because of these properties the entropy is a so-called *thermodynamic potential* (later on we will become acquainted with other "potentials" with similar properties). Just like the potential energy of mechanics, the entropy gives information about the most stable (equilibrium) position of the system. And just as with differences in potential energy, entropy differences are the reason why a process happens in an isolated system. Finally, the knowledge of the state function $S(U, N, V, \ldots)$ or equivalently $U(S, N, V, \ldots)$ contains also the knowledge of the main equations of state of a system.

The extensive state variables U, S, V, N, ... are very useful for isolated systems, where they assume constant values in equilibrium, but in practice, for instance in a heat bath, these state variables are often not appropriate. It is, for example, experimentally far easier to control, instead of the entropy, the corresponding intensive variable, the temperature. Quite analogously, in many cases one might prefer the pressure (e.g., atmospheric pressure) as the variable instead of the volume, etc. Therefore it is reasonable to look for other thermodynamic potentials which have quite analogous properties to the entropy or the energy, but which depend on the conjugated intensive variables. Our aim is therefore, for example, in the case of the internal energy $U(S, V, N, \ldots)$, to perform a transformation from the entropy S to the intensive variable $T = (\partial U/\partial S)|_{V,N,\ldots}$.

The transformation we need is the *Legendre transformation*, which is well known from classical mechanics. There one uses this transformation to replace the generalized velocities $\dot{q}_\nu$ in the Lagrange function $L(q_\nu, \dot{q}_\nu)$ by the new variables $p_\nu = \partial L/\partial \dot{q}_\nu$, the generalized momenta. This happens via

$$H(q_\nu, p_\nu) = \sum_\nu \dot{q}_\nu p_\nu - L(q_\nu, \dot{q}_\nu) \tag{4.15}$$

One obtains a function $H(q_\nu, p_\nu)$, which is completely equivalent to $L(q_\nu, \dot{q}_\nu)$ but which depends on the new variable p_ν. The proof is simply given by differentiation:

$$\begin{aligned} dH &= \sum_\nu \left\{ p_\nu \, d\dot{q}_\nu + \dot{q}_\nu \, dp_\nu - \frac{\partial L}{\partial q_\nu} \, dq_\nu - \frac{\partial L}{\partial \dot{q}_\nu} \, d\dot{q}_\nu \right\} \\ &= \sum_\nu \left\{ \dot{q}_\nu \, dp_\nu - \frac{\partial L}{\partial q_\nu} \, dq_\nu \right\} \end{aligned} \tag{4.16}$$

Here only the changes dp_ν and dq_ν occur. We now want to consider the Legendre transformation more extensively in the context of thermodynamics.

The Legendre transformation

Let us first restrict ourselves to functions of one variable. The results are then readily generalized to functions of several variables. Assume $f(x)$ to be a function of the variable x, with the total differential

$$df = \frac{\partial f}{\partial x} \, dx = p(x) \, dx \tag{4.17}$$

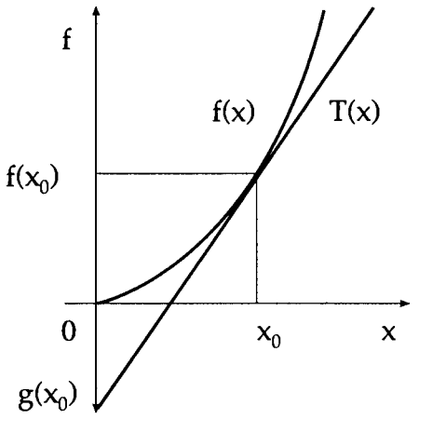


Figure 4.2. Concerning the Legendre transformation.

The function $p(x) = f'(x)$ gives the slope of the curve $f(x)$ for every value of the variable x (let us assume that $f(x)$ is differentiable for all x). The task of the Legendre transformation is to find a function $g(p)$ of the new variable $p = f'(x)$, which is equivalent to the function $f(x)$, i.e., which contains the same information. Thus, one must be able to calculate $g(p)$ unambiguously from the function $f(x)$ and vice versa. The new function $g(p)$ can be readily obtained using the illustrative interpretation in Figure 4.2 of the variable p as slope of the function $f(x)$. To this end, we consider the intersection of the tangent to f at the point $(x_0, f(x_0))$ with the y-axis. The tangent has the following equation:

$$T(x) = f(x_0) + f'(x_0)(x - x_0) \tag{4.18}$$

The intersection with the y-axis $g = T(0)$ therefore is

$$g(x_0) = f(x_0) - x_0 f'(x_0) \tag{4.19}$$

and depends, of course, on the point x_0 under consideration. One calls the function $g(x)$ for an arbitrary point x the *Legendre transform* of $f(x)$; it is

$$g = f - xp \qquad \text{with} \quad p = \frac{\partial f}{\partial x} \tag{4.20}$$

In other words, $g(x)$ is the corresponding value of the intersection of the tangent to f at point $(x, f(x))$ with the y-axis.

We now want to show that g depends solely on the slope $p = f'(x)$. To this end we differentiate Equation (4.20):

$$dg = df - p\,dx - x\,dp \tag{4.21}$$

If one inserts Equation (4.17) for df, one has

$$dg = -x\,dp \tag{4.22}$$

Thus, g can depend only on the variable p. To calculate $g(p)$ explicitly, we have to eliminate x in Equation (4.20),

$$g(x) = f(x) - xf'(x) \tag{4.23}$$

with the help of the equation

$$p = f'(x) \tag{4.24}$$

This, however, is only possible, if Equation (4.24) can be uniquely solved for x, i.e., if there exists the inverse f'^{-1} to f'. Then one can insert

$$x = f'^{-1}(p) \tag{4.25}$$

into Equation (4.23), and one obtains explicitly the function

$$g(p) = f\left(f'^{-1}(p)\right) - f'^{-1}(p)p \tag{4.26}$$

Example 4.2: $f(x) = x^2$

$$f(x) = x^2, \qquad f'(x) = p = 2x \tag{4.27}$$

The Legendre transform reads

$$g(x) = x^2 - px \tag{4.28}$$

The inverse function f'^{-1} exists and can be calculated from Equation (4.27):

$$f'^{-1}(p) = x = \frac{1}{2}p$$

If one inserts this in Equation (4.28), it follows that

$$g(p) = \frac{1}{4}p^2 - \frac{1}{2}p^2 = -\frac{1}{4}p^2$$

The differential reads

$$dg = -\frac{1}{2}p\,dp = -x\,dp$$

which coincides with Equation (4.22).

It is therefore evident that a unique Legendre transform exists only if Equation (4.24) represents a bijective mapping, i.e., if every value of the variable x is uniquely mapped onto a certain value of the slope p and vice versa. From mathematics it is known that the function $f'(x)$ has to be strictly monotonic for Equation (4.24) to be invertible. Thus, only if $f'(x)$ is strictly monotonic does the Legendre transform $g(p)$ exist. If the slope $f'(x)$ is not strictly monotonic, there may be several values of x belonging to a value of the slope p, and the transformation is no longer unique.

Example 4.3: $f(x) = x$

$$f(x) = x, \qquad f'(x) = 1 = p$$

The last equality cannot be solved for x. In particular, the Legendre transform reads (formally)

$$g(x) = x - px = x - x = 0$$

i.e., it does not contain the same information as $f(x)$.

Next we show that one can reconstruct the original function $f(x)$ from the Legendre transform in a unique way. According to Equation (4.20), it holds that

$$f(p) = g(p) + xp \tag{4.29}$$

In this equation we can uniquely replace p by x. According to Equation (4.22), we have

$$x = -g'(p) \tag{4.30}$$

Since $f'(x)$ is strictly monotonous, the inverse function (4.25) is also strictly monotonous. Therefore Equation (4.30) can be uniquely solved for $p(x)$. This can be inserted into Equation (4.29), and we uniquely reobtain the function $f(x)$.

Example 4.4: Reverse transformation

Let us once again consider our first example (4.2). We had

$$g(p) = -\frac{1}{4}p^2$$

If one calculates

$$-x = g'(p) = -\frac{1}{2}p$$

one can solve this for $p(x)$. Equation (4.29) reads in this case

$$f(p) = -\frac{1}{4}p^2 + xp$$

If one here inserts $p(x)$, it follows that

$$f(x) = -x^2 + 2x^2 = x^2$$

which agrees completely with the original function.

The generalization of the Legendre transform to functions of several variables is obvious. For instance, $f(x, y)$ is given. Then the total differential is

$$df = p(x, y)\,dx + q(x, y)\,dy \tag{4.31}$$

where we have put

$$p(x, y) = \left.\frac{\partial f}{\partial x}\right|_y \quad \text{and} \quad q(x, y) = \left.\frac{\partial f}{\partial y}\right|_x \tag{4.32}$$

If the variable x is to be replaced by p, one forms

$$g(x, y) = f(x, y) - xp \tag{4.33}$$

with the total differential

$$\begin{aligned} dg &= df - p\,dx - x\,dp \\ &= -x\,dp + q\,dy \end{aligned} \tag{4.34}$$

where g is only a function of p and y. To calculate $g(p, y)$ explicitly, the first of Equations (4.32) has to be invertible for all values of y. Then one can calculate the function $x(p, y)$

and insert it into Equation (4.33), so that the new function $g(p, y)$ is known. Analogously, one can replace both variables x and y by p and q. To this end, one calculates

$$h(x, y) = f(x, y) - px - qy \tag{4.35}$$

To evaluate $h(p, q)$ explicitly, one must be able to solve the system of equations (4.32) for $x(p, q)$ and $y(p, q)$. Then one can insert these functions into Equation (4.35), and one explicitly obtains the new function $h(p, q)$, which is completely equivalent to the old function $f(x, y)$.

Quite strong presumptions are necessary for the Legendre transform to exist, due to the condition of solvability. One has to check for each special case whether they are fulfilled. However, one can always restrict the domain of the variables to regions where these presumptions are valid; correspondingly one then defines piecewise Legendre transforms. In the next sections we want to study extensively the application of the Legendre transform to thermodynamics.

The free energy

We start from the internal energy $U(S, V, N, ...)$ as a function of the natural variables. The variable S, the entropy, shall be replaced by the temperature $T = \partial U/\partial S|_{V,N,...}$. To this end, one uses the Legendre transform

$$F = U - TS = -pV + \mu N \tag{4.36}$$

which is called the *free energy* or *Helmholtz potential.* Here we have employed Euler's equation (2.72). The total differential of U reads

$$dU = T\,dS - p\,dV + \mu\,dN + \ldots \tag{4.37}$$

Correspondingly, the total differential of F is

$$\begin{aligned} dF &= dU - S\,dT - T\,dS \\ &= -S\,dT - p\,dV + \mu\,dN + \ldots \end{aligned} \tag{4.38}$$

Hence, the free energy is a function of T, V, N, ..., which contains exactly the same information as the internal energy U, but which now depends on the temperature instead of the entropy. In particular one obtains from Equations (4.38) the equations of state

$$-S = \left.\frac{\partial F}{\partial T}\right|_{V,N,...}, \qquad -p = \left.\frac{\partial F}{\partial V}\right|_{T,N,...}, \qquad \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V,...}, \qquad \ldots \tag{4.39}$$

To understand the importance of the free energy we consider a nonisolated system in a heat bath of constant temperature T (Figure 4.3). The total system (including the heat bath) must be isolated. Thus, the second law can be directly applied to the total system. Accordingly,

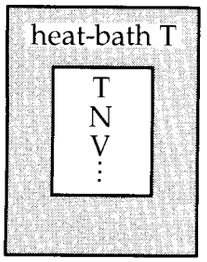


Figure 4.3. Isothermal system.

irreversible processes happen in this total system, until in equilibrium the entropy has a maximum and does not change any more:

$$dS_{\text{tot}} = dS_{\text{sys}} + dS_{\text{bath}} \geq 0 \tag{4.40}$$

Here we have split the total entropy into that of the heat bath and that of the system under consideration.

Since the system and the heat bath are in mutual contact, they may exchange heat and, eventually, also work. This leads, according to the first law, to a change of the internal energy of the partial systems. Let δQ_{sys} be the heat exchanged with the heat bath (as seen from the system) and δA_{sys} the remaining work exchanged with the heat bath. Then we have, according to the first law, for the change in internal energy of the partial systems:

$$dU_{\text{sys}} = \delta Q_{\text{sys}} + \delta W_{\text{sys}}, \qquad dU_{\text{bath}} = \delta Q_{\text{bath}} + \delta W_{\text{bath}} \tag{4.41}$$

Since the total system is isolated, for reversible processes it must hold that

$$\delta Q_{\text{sys}} = -\delta Q_{\text{bath}} \qquad \text{and} \qquad \delta W_{\text{sys}} = -\delta W_{\text{bath}} \tag{4.42}$$

When discussing the second law we have discussed the following inequalities, which are also valid for partial systems:

$$T\,dS = \delta Q_{\text{rev}} \geq \delta Q_{\text{irr}} \qquad \text{and} \qquad \delta W_{\text{rev}} \leq \delta W_{\text{irr}} \tag{4.43}$$

This relation we know already from Equation (2.50). As seen from the system we therefore have

$$dU_{\text{sys}} - T\,dS_{\text{sys}} = \delta W_{\text{sys}}^{\text{rev}} \leq \delta W_{\text{sys}}^{\text{irr}} \tag{4.44}$$

For a given *constant* temperature we may also write this as follows:

$$dF_{\text{sys}} = d(U_{\text{sys}} - TS_{\text{sys}}) = \delta W_{\text{sys}}^{\text{rev}} \leq \delta W_{\text{sys}}^{\text{irr}} \tag{4.45}$$

The change of the free energy dF_{sys} of the system at *constant temperature* (isothermal process) represents the work done by or performed on the system in a *reversible process*. This work is always smaller (including sign) than that in irreversible processes.

For reversible processes the equality sign holds in Equation (4.40), so that with $dU_{\text{sys}} = T\,dS_{\text{sys}} + \delta W_{\text{sys}}^{\text{rev}}$:

$$dS_{\text{bath}} = -dS_{\text{sys}} = -\frac{\delta Q_{\text{sys}}}{T} = -\frac{1}{T}\left(dU_{\text{sys}} - \delta W_{\text{sys}}^{\text{rev}}\right) \tag{4.46}$$

If we insert this into Equation (4.40), it follows for *isothermal reversible* processes ($dS_{\text{tot}} = 0$) that

$$\begin{aligned} T\,dS_{\text{tot}} &= T\,dS_{\text{sys}} - dU_{\text{sys}} + \delta W_{\text{sys}}^{\text{rev}} \\ &= -dF_{\text{sys}} + \delta W_{\text{sys}}^{\text{rev}} = 0 \end{aligned} \tag{4.47}$$

or for irreversible processes, respectively,

$$T\,dS_{\text{tot}} = -dF_{\text{sys}} + \delta W_{\text{sys}}^{\text{irr}} \geq 0 \tag{4.48}$$

Here it becomes quite evident that for isothermal systems the free energy has an importance quite analogous to the entropy for isolated systems. Let the work performed be $\delta W_{\text{sys}} = 0$, then the entropy of the isolated total system has a maximum if and only if the free energy of the isothermal partial system has a minimum. In particular, processes which diminish the free energy happen spontaneously and irreversibly in an isothermal system. Since

$$dF = d(U - TS) = dU - T\,dS \leq 0 \qquad \text{for} \quad \delta W = 0 \text{ and } T = const. \tag{4.49}$$

the free energy yields a combination of the principle of maximum entropy and minimum energy. Isothermal systems, which can exchange only heat, but not work with their surroundings, try to minimize their free energy; i.e., they try to minimize their energy and simultaneously maximize their entropy! This has the consequence that, for instance, isothermal processes which actually increase the internal energy, i.e., which require energy input, nevertheless happen spontaneously, if for a given temperature the gain in entropy TdS is larger than the expense in energy dU—the energy is here extracted from the heat bath.

In general, an isothermal system which does not exchange work with its surroundings strives for a minimum of the free energy. Irreversible processes happen spontaneously, until the minimum

$$dF = 0, \qquad F = F_{\min} \tag{4.50}$$

is reached.

Example 4.5: Precipitation from a solution

The precipitation of magnesium carbonate from a hydrous solution when mixing solutions which contain separately magnesium ions and carbonate ions,

$$Mg^{2+}_{aq} + CO^{2-}_{3\,aq} \rightarrow MgCO_{3\,solid}$$

happens spontaneously, since the cost in energy $\Delta U \approx 25.1$ kJ/mol is much smaller than the gain in entropy, which is approximately $T\,\Delta S \approx 71.1$ kJ/mol at room temperature. This example shows that one has to be very careful in the probabilistic interpretation of the entropy. The conglomeration of Mg and CO_3 ions to a solid seems to correspond to a decrease in entropy compared to the homogeneous distribution of the ions in the solution. However, as the measurement of ΔU and ΔS shows, this is not the case. The reason is that ions in a hydrous solution are surrounded by a systematic hydrate envelope of water molecules. The break-up of this well-ordered hydrate envelope again yields a larger gain in entropy than the conglomeration of the ions to a solid.

Analogously, processes at constant temperature, for which the decrease of the internal energy is larger than the decrease of the entropy, also happen spontaneously. And of course, processes happen spontaneously which increase the entropy as well as decrease the energy.

The application of the free energy is not restricted to isothermal systems. In these cases their interpretation is only very obvious. The free energy can in principle be calculated for

any system from the internal energy by means of a Legendre transformation. It is completely equivalent to the internal energy. In particular, one can calculate from the free energy the internal energy, as well as all equations of state. Therefore it is a thermodynamic potential.

Example 4.6: Free energy of the ideal gas

We want to calculate the free energy of the ideal gas. To this end we solve Equation (4.10) for $U(S, V, N)$,

$$U(S, V, N) = U_0 \left(\frac{N}{N_0}\right)^{5/3} \left(\frac{V_0}{V}\right)^{2/3} \exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - s_0\right)\right\} \tag{4.51}$$

Now we form

$$F = U - TS \tag{4.52}$$

To obtain $F(T, V, N)$ we have to express S in Equation (4.52) by T. This happens via

$$T = \left.\frac{\partial U}{\partial S}\right|_{N,V,\ldots} = U_0 \left(\frac{N}{N_0}\right)^{5/3} \left(\frac{V_0}{V}\right)^{2/3} \times \exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - s_0\right)\right\} \frac{2}{3Nk}$$

This equation has to be solved for $S(T, V, N)$:

$$S(T, V, N) = Nk\left[s_0 + \ln\left\{\left(\frac{3}{2}\frac{NkT}{U_0}\right)^{3/2}\left(\frac{N_0}{N}\right)^{5/2}\left(\frac{V}{V_0}\right)\right\}\right]$$

If we insert this into Equation (4.52) for S, it follows that

$$F(T, V, N) = \frac{3}{2}NkT - NkT\left[s_0 + \ln\left\{\left(\frac{3}{2}\frac{NkT}{U_0}\right)^{3/2}\left(\frac{N_0}{N}\right)^{5/2}\left(\frac{V}{V_0}\right)\right\}\right]$$

or, with $U_0 = \frac{3}{2}N_0kT_0$, that

$$F(T, V, N) = NkT\left[\frac{3}{2} - s_0 - \ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{N_0}{N}\right)\left(\frac{V}{V_0}\right)\right\}\right] \tag{4.53}$$

where s_0 is again the constant which fixes the scale of entropy. Together with T_0, N_0, and V_0 this constant yields the free energy $F_0(T_0, V_0, N_0)$ in the reference state, so that as usual in thermodynamics, Equation (4.53) represents only a difference compared to a reference state.

Now we show that $F(T, V, N)$, as well as $U(S, V, N)$ or $S(U, V, N)$, contains all the equations of state. To this end we just have to calculate the partial derivatives of F with respect to the variables:

$$S(T, V, N) = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = Nk\left[s_0 + \ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{N_0}{N}\right)\left(\frac{V}{V_0}\right)\right\}\right] \tag{4.54}$$

$$p(T, V, N) = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{NkT}{V} \tag{4.55}$$

$$\mu(T, V, N) = \left.\frac{\partial F}{\partial N}\right|_{T,V} = kT\left[\frac{5}{2} - s_0 - \ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{N_0}{N}\right)\left(\frac{V}{V_0}\right)\right\}\right] \quad (4.56)$$

Together with the reverse transformation,

$$U(T, V, N) = F(T, V, N) + TS = \frac{3}{2}NkT \quad (4.57)$$

the free energy is completely equivalent to $S(U, V, N)$ or to $U(S, V, N)$, which follows immediately after eliminating the corresponding variables in Equations (4.54–56).

At the end of this section we want to illustrate the qualitative difference between internal energy and free energy. It is, of course, possible to rewrite the internal energy $U(S, V, N)$ of an ideal gas directly in terms of other variables with the help of the equations of state. For instance, $U(T, V, N)$ is well known to us,

$$U(T, V, N) = \frac{3}{2}NkT \quad (4.58)$$

Note, however, that $U(T, V, N)$ is a different physical quantity than $F(T, V, N)$, as one readily confirms by comparison with Equation (4.57). In an isothermal system, for instance, the free energy has a minimum in equilibrium, but not necessarily the internal energy. The difference is that $F(T, V, N)$ contains the full thermodynamic information about the system, as well as $U(S, V, N)$. By contrast, in $U(T, V, N)$ information was lost. One cannot determine the entropy from $U(T, V, N)$ without the help of other equations of state, while this is possible for the free energy via $-S = \left.\frac{\partial F}{\partial T}\right|_{V,N}$.

The enthalpy

After extensively discussing the principle of the Legendre transformation for the free energy and the pair of variables T and S, it is not difficult to transfer this method also to other pairs of variables. In chemistry, processes at constant (atmospheric) pressure are of special interest, since usually chemical reactions happen in open vessels, i.e., under the direct influence of the atmosheric pressure. (See Figure 4.4.) Therefore, we want to transform the internal energy $U(S, V, N, \ldots)$ from the variable V to the new variable p. Since the term $-p\,dV$ in the differential of U occurs with a negative sign, we also have to change the sign in the Legendre transformation:

$$H = U + pV = TS + \mu N \quad (4.59)$$

Equation (4.59) defines the *enthalpy*, which is also a thermodynamic potential, in the variables S, p and N. The total differential of the enthalpy reads

$$\begin{aligned} dH &= dU + p\,dV + V\,dp \\ &= T\,dS + V\,dp + \mu\,dN + \ldots \end{aligned} \quad (4.60)$$

If the enthalpy $H(S, p, N, \ldots)$ is known, all other state quantities may be obtained by partial differentiation, as for U and F,

$$T = \left.\frac{\partial H}{\partial S}\right|_{p,N,\ldots}, \qquad V = \left.\frac{\partial H}{\partial p}\right|_{S,N,\ldots}, \qquad \mu = \left.\frac{\partial H}{\partial N}\right|_{S,p,\ldots}, \qquad \ldots \tag{4.61}$$

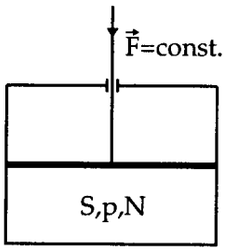


Figure 4.4. Isobaric system (p = const.). If heat exchange with the surroundings is prevented, the system is also adiabatic.

As with all other thermodynamic potentials the enthalpy can in principle be calculated for any system. However, it is especially useful for isobaric (p = const., $dp = 0$) and adiabatic ($\delta Q = 0$) systems. Such systems do not exchange heat with their surroundings, but can perform volume work against the constant external pressure in an expansion ($\delta W_{\text{vol}}^{\text{rev}} = -p\,dV$), and may furthermore exchange other forms of work with their surroundings (e.g., $\delta W_{\text{other}}^{\text{rev}} = \mu dN$, etc.). Thus, the total work reversibly exchanged with the surroundings is $\delta W_{\text{tot}}^{\text{rev}} = \delta W_{\text{vol}}^{\text{rev}} + \delta W_{\text{other}}^{\text{rev}}$.

Especially for isobaric systems (p = const., $dp = 0$) we find with the help of the first law, $dU = \delta Q + \delta W = \delta Q + \delta W_{\text{other}} - pdV$, for reversible changes of state at constant pressure, that

$$dH|_p = d(U + pV)|_p = (dU + pdV + Vdp)_p = dU|_p + pdV|_p$$

$$dH|_p = \delta Q|_p + \delta W_{\text{other}}^{\text{rev}}|_p \tag{4.62}$$

For isobaric changes of state, the change of the enthalpy is just the amount of heat exchanged with the surroundings plus the exchanged utilizable work, which is not simply volume work against the constant external pressure. If the system does not perform such utilizable work in the change of state under consideration (or if there is no such work to be performed on the system), we have $dH|_p = \delta Q|_p$. In this case, the enthalpy difference gives the amount of heat exchanged with the surroundings at constant pressure. On the other hand, by measuring such amounts of heat one can determine enthalpy differences. By the way, this is quite analogous to the statement $dU|_V = \delta Q|_V$ in systems at constant volume which do not exchange work with their surroundings ($dU = \delta Q + \delta W$, $\delta W = 0$). Then the exchanged amount of heat is identical with the change of the internal energy.

Let us consider especially an isobaric and adiabatic system with p = const. and $\delta Q = 0$. Then we have according to Equation (4.62)

$$dH|_{p,ad} = \delta W_{\text{other}}^{\text{rev}}|_{p,ad} \tag{4.63}$$

The change of enthalpy for an isobaric, adiabatic change of state is the utilizable work reversibly gained from (or required by) the system aside from the volume work. This statement corresponds to Equation (4.45) for the change of the free energy in an isothermal system. Again, for irreversible processes $\delta W_{\text{other}}^{\text{rev}} \leq \delta W_{\text{other}}^{\text{irr}}$ is valid and thus

$$dH|_{p,ad} = \delta W_{\text{other}}^{\text{rev}}|_{p,ad} \leq \delta W_{\text{other}}^{irr}|_{p,ad} \tag{4.64}$$

For irreversible processes the maximum possible utilizable work, namely the reversible work, is not performed. If, especially for an irreversible process in the isobaric, adiabatic system $\delta W_{\text{other}}^{\text{irr}} = 0$, i.e., if no utilizable work is performed, we have

$$dH \leq 0 \tag{4.65}$$

In an adiabatic, isobaric system, which is left to its own, irreversible processes happen, which decrease the enthalpy, until in equilibrium a minimum of the enthalpy is reached,

$$dH = 0, \qquad H = H_{\min} \tag{4.66}$$

The enthalpy is thus very similar to the internal energy. In a system under constant pressure, however, most changes of state require volume work, which is explicitly considered in the enthalpy.

Example 4.7: Enthalpy of the ideal gas

We start again from Equation (4.51) and form

$$H = U + pV \tag{4.67}$$

To calculate $H(S, p, N)$ explicitly we have to eliminate V, with the help of Equation (4.51), according to

$$-p = \left.\frac{\partial U}{\partial V}\right|_{S,N,\ldots} = -\frac{2}{3}U_0\left(\frac{N}{N_0}\right)^{5/3}\frac{V_0^{2/3}}{V^{5/3}}\exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - s_0\right)\right\} \tag{4.68}$$

Equation (4.68) has to be solved for V and inserted into Equation (4.67). First, we have

$$\frac{V}{V_0} = \left(\frac{2}{3}\frac{U_0}{pV_0}\right)^{3/5}\left(\frac{N}{N_0}\right)\exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\}$$

If one inserts this into Equation (4.67), one gets

$$H(S, p, N) = U_0\left(\frac{N}{N_0}\right)\left(\frac{2}{3}\frac{U_0}{pV_0}\right)^{-2/5}\exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\} + pV_0\left(\frac{2}{3}\frac{U_0}{pV_0}\right)^{3/5}\left(\frac{N}{N_0}\right)\exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\}$$

If one combines both terms, it holds that

$$H(S, p, N) = \frac{5}{3}U_0\left(\frac{N}{N_0}\right)\left(\frac{2}{3}\frac{U_0}{pV_0}\right)^{-2/5}\exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\}$$

With $U_0 = \frac{3}{2}N_0kT_0 = \frac{3}{2}p_0V_0$ we may write the constants also as follows:

$$H(S, p, N) = \frac{5}{3}U_0\left(\frac{N}{N_0}\right)\left(\frac{p}{p_0}\right)^{2/5}\exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\} \tag{4.69}$$

As usual, the enthalpy is only determined up to an additive constant, which can be chosen in a way that, for $S = Nks_0$, $N = N_0$, and $p = p_0$, H assumes the value $H_0 = \frac{5}{3}U_0$.

Exercise 4.8: Calculation of the equations of state from the enthalpy

Show that Equations (4.61) with the enthalpy of the ideal gas, Equation (4.69), yield the equations of state of the ideal gas.

Solution We have

$$T(S, p, N) = \left.\frac{\partial H}{\partial S}\right|_{p,N}$$

$$= \frac{2U_0}{3N_0k}\left(\frac{p}{p_0}\right)^{2/5} \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\} \tag{4.70}$$

$$V(S, p, N) = \left.\frac{\partial H}{\partial p}\right|_{S,N}$$

$$= \frac{2U_0}{3p_0}\left(\frac{N}{N_0}\right)\left(\frac{p}{p_0}\right)^{-3/5} \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\} \tag{4.71}$$

If one eliminates S from Equations (4.70) and (4.71) by dividing both equations, it follows that

$$\frac{V}{T} = \frac{Nk}{p}$$

which is the ideal gas law. Similarly one can obtain the internal energy by the reverse transformation

$$U = H - pV$$

If one multiplies Equation (4.71) by p and subtracts this from Equation (4.69), one has

$$U(S, p, N) = U_0\left(\frac{N}{N_0}\right)\left(\frac{p}{p_0}\right)^{2/5} \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\}$$

If one substitutes Equation (4.70) for the last two factors, one has

$$U(T, V, N) = U_0 \frac{N}{N_0}\frac{3}{2}\frac{N_0kT}{U_0} = \frac{3}{2}NkT$$

i.e., the correct internal energy of the ideal gas, which can of course be rewritten as $U(S, V, N)$. Finally, the chemical potential is given by

$$\mu = \left.\frac{\partial H}{\partial N}\right|_{S,p} = \frac{5U_0}{3N_0}\left(1 - \frac{2S}{5Nk}\right)\left(\frac{p}{p_0}\right)^{2/5} \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\}$$

We eliminate the last two factors with Equation (4.70):

$$\mu = \frac{5}{2}kT\left(1 - \frac{2S}{5Nk}\right) \tag{4.72}$$

If one solves Equation (4.70) for $S(N, p, T)$ and inserts this into Equation (4.72), one has, with $U_0 = \frac{3}{2}N_0kT_0$,

$$\mu(p, T) = kT\left[\frac{5}{2} - s_0 - \ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\}\right]$$

which again agrees with the chemical potential of the ideal gas formerly calculated, if $\mu_0(p_0, T_0) = kT_0(\frac{5}{2} - s_0)$.

With the help of the enthalpy we want to demonstrate the usefulness of various thermodynamic potentials for special systems. If we add an amount of heat δQ to a system at constant volume, we have, with $\delta W = 0$,

$$dU = \delta Q|_V \tag{4.73}$$

so that the amount of heat directly increases the internal energy. For the specific heat at constant volume it holds that

$$C_V = \left.\frac{\delta Q}{dT}\right|_V = \left.\frac{\partial U}{\partial T}\right|_V \tag{4.74}$$

However, if the heat δQ is added under constant pressure, generally the volume of the system will change, and a certain volume work will be performed:

$$dU = \delta Q|_p - p\,dV \tag{4.75}$$

The internal energy is not very appropriate for describing this process, since not only the temperature, but also the volume of the system changes. At constant pressure, however, Equation (4.75) can be simply put in the form

$$dH = d(U + pV) = \delta Q|_p \tag{4.76}$$

which is quite analogous to Equation (4.73). The specific heat at constant pressure therefore is

$$C_p = \left.\frac{\delta Q}{dT}\right|_p = \left.\frac{\partial H}{\partial T}\right|_p \tag{4.77}$$

If we rewrite Equation (4.69) with the help of Equation (4.70) as $H(T, p, N)$, we have for an ideal gas

$$H(T, p, N) = \frac{5}{2}NkT \tag{4.78}$$

which also follows directly from $H = U + pV = \frac{3}{2}NkT + NkT$. Thus we obtain for an ideal gas

$$C_p = \frac{5}{2}Nk \tag{4.79}$$

while

$$C_V = \frac{3}{2}Nk \tag{4.80}$$

The specific heat at constant pressure is larger than that at constant volume by Nk, since a part of the heat $\delta Q|_p$ is transformed into volume work against the external pressure p.

In chemistry the enthalpy plays an important role, since many chemical reactions happen in open vessels at constant pressure. On the other hand, many reactions happen so fast that an exchange of heat with the surroundings is nearly impossible ($\delta Q = 0$). With the help of the enthalpy one can very easily decide in this case whether a certain chemical reaction is possible and whether it happens spontaneously under given conditions (e.g.,

atmospheric pressure, room temperature). To this end, one simply compares the sum of the enthalpies of the reaction products with that of the reactants. If $\Delta H = H_{\text{products}} - H_{\text{reactants}}$ is negative, i.e., $\Delta H \leq 0$, the reaction happens spontaneously and irreversibly. To simplify such a comparison, pure chemical elements at room temperature and atmospheric pressure have by definition the enthalpy $H_0(p_0, T_0) = 0$, so that the arbitrary additive constant is determined. However, for chemical reactions the restrictiveness of thermodynamics also becomes clear. In most cases a certain activation energy is necessary for a reaction; i.e., the reaction happens spontaneously and yields a gain in enthalpy, but is restrained by an energy barrier which first must be overcome. About these phenomena belonging to the reaction dynamics thermodynamics cannot make any assertions. Reactions which happen under constant pressure and where enthalpy is released are called *exothermal*, while reactions which enlarge the enthalpy, i.e., which only happen if work is performed, are called *endothermal*.

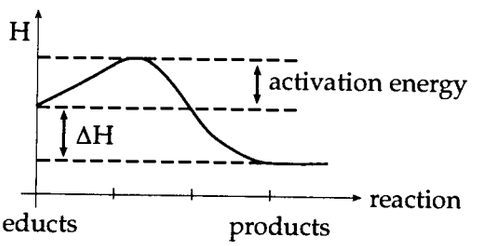


Figure 4.5. Enthalpy during a chemical reaction.

In Figure 4.5 the typical course of the enthalpy is plotted against a qualitative reaction coordinate (e.g., the concentration of the products) for a typical exothermal reaction (e.g., combustion of H_2 with O_2 to produce H_2O). The activation energy is necessary to break up the H_2 and O_2 molecules, which only then can form the H_2O molecules. Here an enthalpy ΔH is effectively released. The measurement of reaction enthalpies in chemistry is simply done by measuring the amount of heat released in the reaction via a calorimeter. It is $dH = \delta Q|_p$; therefore, if one adds the amount of heat δQ under constant pressure, e.g., to a water bath of known heat capacity, one can measure the reaction enthalpy by determining the increase of temperature. Since the enthalpy is a state quantity, the way in which a reaction product is created plays no role. One always obtains the same difference in enthalpy.

Example 4.9: Reaction enthalpy

For instance, if carbon is combusted together with oxygen, carbon dioxide is formed according to the equation

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -394\ \text{kJ/mol}$$

However, this reaction can also be performed in two partial steps:

$$C + \frac{1}{2} O_2 \rightarrow CO \qquad \Delta H = -111\ \text{kJ/mol}$$

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \qquad \Delta H = -283\ \text{kJ/mol}.$$

Here carbon monoxide is created in the first step. The total balance of enthalpy, however, is in both cases identical. The assertion that the total enthalpy difference between the products and the reactants does not depend on the course of the reaction, is sometimes also called the *Theorem of Hess*.

The free enthalpy

For systems with given temperature and pressure we have to perform the Legendre transformation of the internal energy $U(S, V, N, \ldots)$ with respect to two variables, namely S and V:

$$G = U - TS + pV \tag{4.81}$$

The corresponding thermodynamic potential is the free enthalpy introduced by J.W. Gibbs (1875), for which reason it is also called the *Gibbs' potential.* The total differential of the free enthalpy reads

$$\begin{aligned} dG &= dU - T\,dS - S\,dT + p\,dV + V\,dp \\ &= -S\,dT + V\,dp + \mu\,dN + \ldots \end{aligned} \tag{4.82}$$

Consequently, G indeed depends only on T, p, and N. If the function $G(T, p, N)$ is known, we can obtain all further quantities by partial differentiation,

$$-S = \left.\frac{\partial G}{\partial T}\right|_{p,N,\ldots}, \qquad V = \left.\frac{\partial G}{\partial p}\right|_{T,N,\ldots}, \qquad \mu = \left.\frac{\partial G}{\partial N}\right|_{T,p,\ldots}, \qquad \ldots \tag{4.83}$$

Equations (4.83) yield again the *equations of state of the system.* Using Euler's equation, which must be fulfilled in any case, we can identify the Gibbs' free enthalpy somewhat more explicitly. Euler's equation (2.72) for a system of one particle species which does not exchange any further kinds of work, reads

$$U = TS - pV + \mu N \tag{4.84}$$

From this follows immediately by comparison with Equation (4.81)

$$G = U - TS + pV = \mu N \tag{4.85}$$

The third of Equations (4.83) is thus trivially fulfilled for the free enthalpy; i.e., $\mu = \partial G/\partial N|_{T,p} = G/N$. Hence, G is directly proportional to the particle number, and *the free enthalpy per particle is identical with the chemical potential.* These statements, however, are only valid for systems consisting of one kind of particle, which cannot exchange other forms of energy (e.g., electrical) with their surroundings. If this is not the case, further terms occur in Euler's equation.

The free enthalpy is especially convenient for systems at a given temperature and given pressure. The quantity represents a combination of free energy (replacement of S by T) and enthalpy (replacement of V by p), a fact, which is expressed also in its name.

To understand the meaning of the free enthalpy, we form an isolated system consisting of the isothermal, isobaric system shown in Figure 4.6 and its surroundings (the heat bath). Then it holds that

$$dS_{\text{tot}} = dS_{\text{sys}} + dS_{\text{bath}} \geq 0 \tag{4.86}$$

The equality sign holds for reversible, the greater-than-or-equal-to sign for irreversible processes. The heat bath, which is of no further interest, can be excluded from the following

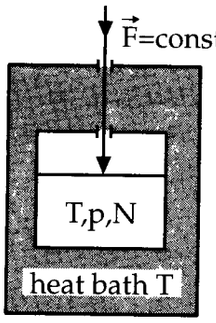


Figure 4.6. Isothermal, isobaric system.

consideration with the help of the first law for *reversible* processes. It holds (for reversible processes) that

$$dS_{\text{bath}} = -dS_{\text{sys}} = -\frac{1}{T}\left(dU_{\text{sys}} + p\,dV_{\text{sys}} - \delta W^{\text{rev}}_{\text{other}}\right) \tag{4.87}$$

or (for irreversible processes), according to Equation (4.86),

$$T\,dS_{\text{tot}} = T\,dS_{\text{sys}} - dU_{\text{sys}} - p\,dV_{\text{sys}} + \delta W^{\text{rev}}_{\text{other}} \geq 0 \tag{4.88}$$

which can also be written as follows (the subscript *sys* is omitted)

$$dG = d(U - TS + pV) = \delta W^{\text{rev}}_{\text{other}} \leq \delta W^{\text{irr}}_{\text{other}} \tag{4.89}$$

The change in the free enthalpy is just the work performed by the system in an isothermal, isobaric *reversible* process, without the volume work against the constant external pressure. Emphasis is put on the *reversibility* of the process: then the equality sign holds in Equations (4.86) and (4.88), and thus it follows that $dG = \delta W^{\text{rev}}_{\text{other}}$. For an irreversible process accordingly less work is released or more work is necessary. This is represented by the inequality in Equation (4.89).

Thus, in an isothermal, isobaric system which is left to its own, irreversible processes happen until a minimum of the free enthalpy is achieved,

$$dG = 0, \qquad G = G_{\min} \tag{4.90}$$

The thermodynamic potential $G(T, p, N)$ is again completely equivalent to the well-known $U(S, V, N)$ or $S(U, V, N)$, respectively, as well as to $F(T, V, N)$ and $H(S, p, N)$, and contains the same information.

Like enthalpy, the free enthalpy is of great importance for chemistry. If chemical reactions happen slowly under constant (atmospheric) pressure, then in practice thermal equilibrium is always maintained; i.e., T = const. This is the case for instance in many fuel cells or batteries. One can therefore directly calculate the electrical work obtainable from a battery as the difference of the free enthalpies in the final and the initial states. Reactions where the free enthalpy decreases, i.e., which happen spontaneously and supply power, are called *exergonic*, while reactions in which the free enthalpy increases are called *endergonic*.

Example 4.10: Free enthalpy of the ideal gas

In principle we do not need to calculate anything, since we have

$$G(T, p, N) = N\mu(T, p)$$

and $\mu(T, p)$ is already known (cf. Example 2.8). However, it is instructive to calculate the free enthalpy via the Legendre transformation and to show that this way yields the same result.

Nevertheless, we do not need to perform the full transformation

$$G = U - TS + pV$$

Rather, it is sufficient to transform the free energy according to

$$G = F + pV$$

In the case of an ideal gas this is particularly simple, because it holds according to Equations (4.53) and (4.55) that

$$G = NkT\left[\frac{3}{2} - s_0 - \ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{N_0}{N}\right)\left(\frac{V}{V_0}\right)\right\}\right] + NkT$$

$$= NkT\left[\frac{5}{2} - s_0 - \ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\}\right]$$

This agrees indeed with $\mu(p, T)$ from Example 2.8, up to a factor N, if $\mu_0(p_0, T_0) = kT_0(\frac{5}{2} - s_0)$.

Exercise 4.11: Gibbs–Helmholtz equation

Show that the free enthalpy and its derivative with respect to temperature can be related to the enthalpy of the system via the *Gibbs–Helmholtz equation*

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_p = -T^2\left(\frac{\partial (G/T)}{\partial T}\right)_p$$

Solution We start from the definitions of the enthalpy $H(S, p, N)$ and the free enthalpy $G(T, p, N)$. We have, using Equation (4.89)

$$H = U + pV = TS + \mu N \tag{4.91}$$

and

$$G = U + pV - TS \tag{4.92}$$

From Equations (4.91) and (4.92) it follows immediately that

$$H = G + TS \tag{4.93}$$

For the total derivative of Equation (4.92)

$$dG = dU - TdS - SdT + pdV + Vdp$$

it follows, with $dU = TdS - pdV + \mu dN$, that

$$dG = -SdT + Vdp + \mu dN$$

Furthermore it holds that

$$dG = \left.\frac{\partial G}{\partial T}\right|_{p,N} dT + \left.\frac{\partial G}{\partial p}\right|_{T,N} dp + \left.\frac{\partial G}{\partial N}\right|_{T,p} dN$$

Comparing coefficients it follows that

$$S = -\left.\frac{\partial G}{\partial T}\right|_{p,N}$$

If we insert this into Equation (4.93) it follows that

$$H = G - T \left.\frac{\partial G}{\partial T}\right|_{p,N} \tag{4.94}$$

It also holds that

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\Big|_{p,N} = \frac{1}{T}\left.\frac{\partial G}{\partial T}\right|_{p,N} - \frac{G}{T^2} = -\frac{1}{T^2}\left[G - T\left.\frac{\partial G}{\partial T}\right|_{p,N}\right]$$

Thus Equation (4.94) becomes

$$H = -T^2 \frac{\partial}{\partial T}\left(\frac{G}{T}\right)\Big|_{p,N}$$

If the isothermal, isobaric system consists of several chemical components (particle species), then it holds according to the extended Euler equation (2.72), that

$$G = \sum_i \mu_i N_i \tag{4.95}$$

If reactions between the particles are possible,

$$a_1 A_1 + a_2 A_2 + \ldots \rightleftharpoons b_1 B_1 + b_2 B_2 + \ldots \tag{4.96}$$

then for the changes in the particle numbers dN_{A_i} of species A_i and dN_{B_j} of species B_j, the relations $dN_{A_i} = -a_i\, dN$ and $dN_{B_j} = b_j\, dN$ have to be valid, where dN is a common factor (e.g., a change by one particle). Therefore we can write the equilibrium condition for an *isothermal, isobaric system*,

$$dG = \sum_i \mu_i\, dN_i = 0 \tag{4.97}$$

also, it follows that

$$dG = \left(-\sum_i \mu_{A_i} a_i + \sum_j \mu_{B_j} b_j\right) dN = 0 \tag{4.98}$$

Since the common factor dN is arbitrary, we must have

$$\sum_i \mu_{A_i} a_i = \sum_j \mu_{B_j} b_j \tag{4.99}$$

a relation which we had derived earlier from other considerations (cf. Equation (3.10)). We already know the dependence of the chemical potential on concentration in dilute solutions or gases (cf. Equation (3.32) and Exercise 3.3),

$$\mu_i(p, T, X_i) = \mu_i^0(p, T) + kT \ln X_i \tag{4.100}$$

Here X_i is the molar fraction of component i and μ_i^0 is the chemical potential of component i in a reference state (e.g., $X_i = 1$). If we insert this into Equation (4.98) we have

$$dG = \left(\sum_j \mu_{B_j}^0 b_j - \sum_i \mu_{A_i}^0 a_i \right) dN + kT \ln \left\{ \frac{(X_{B_1})^{b_1} (X_{B_2})^{b_2} \cdots}{(X_{A_1})^{a_1} (X_{A_2})^{a_2} \cdots} \right\} dN \tag{4.101}$$

Since $\partial G/\partial N = G/N$; i.e., it is independent of the change in the particle number dN, we can put $dN = 1$ and obtain

$$\Delta G(p, T, X_{A_1}, \ldots, X_{B_1}, \ldots) = \Delta G^0(p, T) + kT \ln \left\{ \frac{(X_{B_1})^{b_1} (X_{B_2})^{b_2} \cdots}{(X_{A_1})^{a_1} (X_{A_2})^{a_2} \cdots} \right\} \tag{4.102}$$

The quantity $\Delta G^0(p, T)$ is a characteristic constant for the reaction (4.96) which depends on pressure and temperature. In equilibrium we must have $\Delta G = 0$, or

$$\frac{(X_{B_1})^{b_1} (X_{B_2})^{b_2} \cdots}{(X_{A_1})^{a_1} (X_{A_2})^{a_2} \cdots} = \exp \left\{ - \frac{\Delta G^0(p, T)}{kT} \right\} \tag{4.103}$$

We observe that the equilibrium condition $\Delta G = 0$ for an isothermal, isobaric system leads directly to the law of mass action. In particular, we now have identified the equilibrium constant more explicitly. It is determined by the free enthalpy difference ΔG^0 between the products and the reactants at standard concentration.

For exergonic reactions with $\Delta G^0 < 0$ the concentrations of the products will be much larger in equilibrium. If one increases the temperature in this case, the absolute value of $\Delta G^0/kT$ becomes smaller and the equilibrium is shifted in favor of the reactants. Analogously, an increase of the pressure shifts the equilibrium in favor of the side which has the smaller volume. Thus, Equation (4.103) contains also an exact formulation of the *principle of Le Chatelier*, according to which an equilibrium state changes under exertion of a force (temperature change, pressure change, or change of concentration) in such a manner that the system gives way to the force.

We define the equilibrium constant appearing in Equation (4.103)

$$K(p, T) = \exp \left\{ - \frac{\Delta G^0(p, T)}{kT} \right\} \tag{4.104}$$

We can calculate quite generally the dependence of the equilibrium constant on pressure and temperature. Using the free reaction enthalpy per particle

$$\Delta G^0(p, T) = \sum_j \mu_j^0 b_j - \sum_i \mu_i^0 a_i \tag{4.105}$$

we obtain

$$\left.\frac{\partial \ln K(p,T)}{\partial p}\right|_T = -\frac{\Delta v}{kT} \tag{4.106}$$

if we denote the change of the volume per particle at a given p and T by

$$\begin{aligned}\Delta v &= \frac{\partial}{\partial p}\left(\sum_j \mu_j^0 b_j - \sum_i \mu_i^0 a_i\right)\Big|_T \\ &= \sum_j v_j^0 b_j - \sum_i v_i^0 a_i\end{aligned} \tag{4.107}$$

For instance, $v = kT/p$ for an ideal gas. Thus, if there are more particles produced in the reaction than were originally present, we have $\Delta v > 0$, since more particles occupy more volume at a given T and p. Then, the righthand side in Equation (4.106) is negative and the equilibrium constant decreases with increasing pressure. Thus, the equilibrium state is shifted in favor of the reactants, since they occupy a smaller volume. Equation (4.106) was first stated by Planck and van Laar. Of course, one can multiply by 1 mol $= N_A$ and write $\Delta v \cdot N_A$ for the change of the molar volume. Then the gas constant $N_A k = R$ appears in the denominator.

In the same manner we find for the temperature dependence of the equilibrium constant

$$\left.\frac{\partial \ln K(p,T)}{\partial T}\right|_p = \frac{\Delta h}{kT^2} \tag{4.108}$$

if we denote the reaction enthalpy per particle by Δh. We have

$$\Delta h = -T^2 \frac{\partial}{\partial T}\left(\sum_j b_j \frac{\mu_j^0}{T} - \sum_i a_i \frac{\mu_i^0}{T}\right)\Big|_p \tag{4.109}$$

because it holds in general, according to the Gibbs–Duhem relation, that

$$\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right)\Big|_p = -\frac{\mu}{T^2} - \frac{s}{T} \tag{4.110}$$

due to $\partial\mu/\partial T|_p = -s = -S/N$, and furthermore $H = U + pV = \mu N + TS$. Hence $h = H/N = \mu + Ts$ is the enthalpy per particle. Equation (4.108) was derived by van't Hoff. It describes the change of the equilibrium constant for a change of temperature, if the reaction enthalpy per particle (or again, per mole) is known. If for example, $\Delta h > 0$, i.e., if one requires energy for the reaction at constant pressure and constant entropy (no heat exchange), the righthand side of Equation (4.108) is positive and the equilibrium constant increases with increasing temperature. Thus, for increasing temperature the equilibrium shifts toward the products for reactions which consume energy. Analogous considerations hold for $\Delta h < 0$.

In our present considerations we have concentrated on chemistry. If, however, one considers reactions of elementary particles in a hot star or in a plasma instead of a chemical reaction, the fundamental principles remain the same, only the notations and the equations of state are changed.

The grand potential

To complete the survey on thermodynamic potentials we now consider systems, where the chemical potential is given as a state variable, instead of the particle number N as in the previous cases. Just as a fixed temperature is established by a heat bath, the chemical potential can be fixed via a particle bath. Just as the exchange of heat with a heat bath leads to a constant temperature in equilibrium, the exchange of particles with a particle reservoir leads to a constant chemical potential. Since such a particle exchange is in most cases also connected with a heat exchange and the particle reservoir thus also acts like a heat bath, we want to transform the internal energy in the variables S and N to the new variables T and μ,

$$\Phi = U - TS - \mu N \tag{4.111}$$

The corresponding potential is called the *grand potential*. It is of great importance for the statistical treatment of thermodynamic problems. The total differential reads

$$\begin{aligned} d\Phi &= dU - T\,dS - S\,dT - \mu\,dN - N\,d\mu \\ &= -S\,dT - p\,dV - N\,d\mu \end{aligned} \tag{4.112}$$

The remaining thermodynamic quantities can be calculated by differentiating the grand potential:

$$-S = \left.\frac{\partial \Phi}{\partial T}\right|_{V,\mu}, \qquad -p = \left.\frac{\partial \Phi}{\partial V}\right|_{T,\mu}, \qquad -N = \left.\frac{\partial \Phi}{\partial \mu}\right|_{T,V} \tag{4.113}$$

Because of Euler's equation

$$U = TS - pV + \mu N \tag{4.114}$$

the grand potential is identical with $-pV$

$$\Phi = -pV \tag{4.115}$$

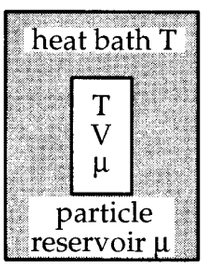


Figure 4.7. Isothermal system with fixed chemical potential.

This potential is especially suited for isothermal systems with a fixed chemical potential (Figure 4.7). If we combine the heat bath and the system under consideration to a total, isolated system, for this system it must hold that

$$dS_{\text{tot}} = dS_{\text{sys}} + dS_{\text{bath}} \geq 0 \tag{4.116}$$

for reversible or irreversible processes, respectively. In the reversible case we can express dS_{bath} by changes of system quantities:

$$T\,dS_{\text{bath}} = -T\,dS_{\text{sys}} = -\left(dU_{\text{sys}} - \mu\,dN_{\text{sys}} - \delta W^{\text{rev}}_{\text{other}}\right) \tag{4.117}$$

If we insert this into Equation (4.116) and consider that for the work reversibly performed by the system $\delta W^{\text{rev}}_{\text{other}}$ (without the explicitly considered chemical energy) we have $\delta W^{\text{rev}}_{\text{other}} \leq$

$\delta W^{\text{irr}}_{\text{other}}$, we obtain

$$dU_{\text{sys}} - T\,dS_{\text{sys}} - \mu\,dN_{\text{sys}} = \delta W^{\text{rev}}_{\text{other}} \leq \delta W^{\text{irr}}_{\text{other}} \tag{4.118}$$

At constant temperature and constant chemical potential this is equivalent to

$$d\Phi = d(U - TS - \mu N) = \delta W^{\text{rev}}_{\text{other}} \leq \delta W^{\text{irr}}_{\text{other}} \tag{4.119}$$

If we leave the system to its own without performing work, $\delta W = 0$, it strives for a minimum of the grand potential,

$$d\Phi \leq 0 \tag{4.120}$$

which is achieved in equilibrium,

$$d\Phi = 0, \qquad \Phi = \Phi_{\text{min}} \tag{4.121}$$

The transformation of all variables

In the following we consider the effect of transforming all variables in U to the new variables T, p, μ. The Legendre transformation would read

$$\Psi = U - TS + pV - \mu N \tag{4.122}$$

plus eventual further terms, if the system contains several chemical components or requires other state quantities for its description. However, according to Euler's equation it must always hold that

$$U = TS - pV + \mu N \tag{4.123}$$

so that this potential vanishes identically, $\Psi \equiv 0$. We remember that Equation (4.123) was a consequence of the Gibbs–Duhem relation, which establishes a relation between the intensive variables T, p, and μ. According to this it is not at all possible to fix the quantities T, p, and μ independently from each other. We have already explicitly calculated the relation $\mu(p, T)$ for an ideal gas. Thus, for a given pressure and temperature the chemical potential is already fixed, and one can at most fix one other extensive variable. This variable then determines the size of the system. The simultaneous transformation of all variables is thus of no relevance.

The Maxwell relations

A variety of relations between the thermodynamic state variables can be derived from the fact that the thermodynamic potentials U, F, H, and G, as well as Φ, are state functions; i.e., they have exact differentials.

The total differential of the internal energy reads (we now consider only systems which are completely characterized by three state variables),

$$dU = T\,dS - p\,dV + \mu\,dN$$

$$= \left.\frac{\partial U}{\partial S}\right|_{V,N} dS + \left.\frac{\partial U}{\partial V}\right|_{S,N} dV + \left.\frac{\partial U}{\partial N}\right|_{S,V} dN \tag{4.124}$$

Since

$$\frac{\partial}{\partial V}\left(\left.\frac{\partial U}{\partial S}\right|_{V,N}\right)_{S,N} = \frac{\partial}{\partial S}\left(\left.\frac{\partial U}{\partial V}\right|_{S,N}\right)_{V,N} \tag{4.125}$$

it immediately follows, e.g., that

$$\left.\frac{\partial T}{\partial V}\right|_{S,N} = -\left.\frac{\partial p}{\partial S}\right|_{V,N} \tag{4.126}$$

In this manner many relations emerge that may allow for the calculation of unknown quantities from known quantities and which we now want to present in a systematic way. At first it follows from Equation (4.124) that

$$\left.\frac{\partial T}{\partial V}\right|_{S,N} = -\left.\frac{\partial p}{\partial S}\right|_{V,N}, \qquad \left.\frac{\partial T}{\partial N}\right|_{S,V} = \left.\frac{\partial \mu}{\partial S}\right|_{V,N}$$

$$-\left.\frac{\partial p}{\partial N}\right|_{S,V} = \left.\frac{\partial \mu}{\partial V}\right|_{S,N} \tag{4.127}$$

Here the coefficients T, p, and μ in Equation (4.124) are of course to be considered as functions of S, V, and N. Corresponding relations exist for the free energy $F(T, V, N)$:

$$dF = -S\,dT - p\,dV + \mu\,dN \tag{4.128}$$

$$-\left.\frac{\partial S}{\partial V}\right|_{T,N} = -\left.\frac{\partial p}{\partial T}\right|_{V,N}, \qquad -\left.\frac{\partial S}{\partial N}\right|_{T,V} = \left.\frac{\partial \mu}{\partial T}\right|_{V,N}$$

$$-\left.\frac{\partial p}{\partial N}\right|_{T,V} = \left.\frac{\partial \mu}{\partial V}\right|_{T,N} \tag{4.129}$$

Here the coefficients S, p, and μ are functions of the variables T, V, and N. Analogously it holds for the enthalpy $H(S, p, N)$ that

$$dH = T\,dS + V\,dp + \mu\,dN \tag{4.130}$$

$$\left.\frac{\partial T}{\partial p}\right|_{S,N} = \left.\frac{\partial V}{\partial S}\right|_{p,N}, \qquad \left.\frac{\partial T}{\partial N}\right|_{S,p} = \left.\frac{\partial \mu}{\partial S}\right|_{p,N}, \qquad \left.\frac{\partial V}{\partial N}\right|_{S,p} = \left.\frac{\partial \mu}{\partial p}\right|_{S,N} \tag{4.131}$$

The coefficients T, V, and μ are now functions of S, p, N. For the free enthalpy $G(T, p, N)$ one has

$$dG = -S\,dT + V\,dp + \mu\,dN \tag{4.132}$$

$$-\left.\frac{\partial S}{\partial p}\right|_{T,N} = \left.\frac{\partial V}{\partial T}\right|_{p,N}, \qquad -\left.\frac{\partial S}{\partial N}\right|_{T,p} = \left.\frac{\partial \mu}{\partial T}\right|_{p,N}$$

$$\left.\frac{\partial V}{\partial N}\right|_{T,p} = \left.\frac{\partial \mu}{\partial p}\right|_{T,N} \tag{4.133}$$

Finally for the grand potential $\Phi(T, V, \mu)$ we have:

$$d\Phi = -S\,dT - p\,dV - N\,d\mu \tag{4.134}$$

$$\left.\frac{\partial S}{\partial V}\right|_{T,\mu} = \left.\frac{\partial p}{\partial T}\right|_{V,\mu}, \qquad \left.\frac{\partial S}{\partial \mu}\right|_{T,V} = \left.\frac{\partial N}{\partial T}\right|_{V,\mu}, \qquad \left.\frac{\partial p}{\partial \mu}\right|_{T,V} = \left.\frac{\partial N}{\partial V}\right|_{T,\mu} \tag{4.135}$$

Relations (4.127), (4.129), (4.131), (4.133), and (4.135) are called *Maxwell relations*. In the literature one often considers systems with constant particle number ($dN = 0$); thus the number of relations is considerably reduced. However, if there are even more state variables, e.g., a magnetic field and a magnetic dipole moment, further relations have to be added. The plenitude of thermodynamic potentials and Maxwell relations seems to be difficult to survey at first sight. However, there exists a simple device which allows for a quick overlook of the potentials and their variables and which yields the Maxwell relations. This device is the thermodynamic rectangle, which is shown in Figure 4.8.

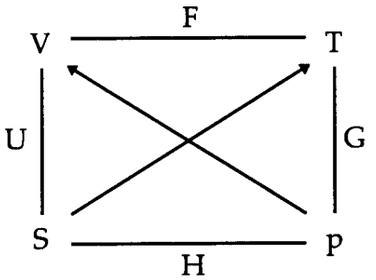


Figure 4.8. Thermodynamic rectangle for N = const.

The thermodynamic rectangle was conceived especially for systems with constant particle number and without further state variables. The variables V, T, p, and S, which are the only possible quantities at constant particle number, form the corners of this quadrangle. Along the edges we denote the potentials, which depend on the variables at the corresponding corners, e.g., $F(V, T)$. With this way of presentation partial derivatives are easily read off. The derivative of a potential with respect to a variable (corner) is just given by the variable at the diagonally opposite corner. The arrows in the diagonals determine the sign.

For instance, we have $\partial F/\partial V = -p$. The minus sign occurs because the direction $V \to p$ is opposite to the direction of the arrow. Analogously we have, e.g., $\partial G/\partial p = +V$. Even the Maxwell relations (now without N) are easy to read off the figure. Derivatives of variables along an edge of the quadrangle (e.g., $\partial V/\partial S$), at constant variable in the diagonally opposite corner (here p), are just equal to the corresponding derivative along the other side, i.e., in this case $\partial T/\partial p|_S$. The signs have to be chosen according to the direction in which one follows the diagonals, e.g., going from V to p yields a minus sign, as does the path $T \to S$.

The usefulness of the Maxwell relations will become immediately clear with the help of some examples.

Example 4.12: Heat capacities

A general relationship shall be established between the heat capacities C_V and C_p, which should, if possible, contain only quantities that are easy to measure.

The definitions of C_V and C_p read (N = const.):

$$C_V = \left.\frac{\delta Q}{dT}\right|_V = T \left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial U}{\partial T}\right|_V$$

$$C_p = \left.\frac{\delta Q}{dT}\right|_p = T \left.\frac{\partial S}{\partial T}\right|_p = \left.\frac{\partial H}{\partial T}\right|_p$$

In the first equation T and V are supposed to be independent variables, while in the second equation T and p are independent. One can write both equations with $S(T, V)$ or $S(T, p)$, respectively, as follows:

$$\delta Q = T\,dS = C_V\,dT + T\left.\frac{\partial S}{\partial V}\right|_T dV \tag{4.136}$$

$$\delta Q = T\,dS = C_p\,dT + T\left.\frac{\partial S}{\partial p}\right|_T dp \tag{4.137}$$

In Equation (4.137) the pressure can as well be regarded as a function of the variables T and V, which are sufficient to determine the state of the system (N = const.). With $p(T, V)$ we can eliminate the differential dp in Equation (4.137) and obtain

$$\delta Q = T\,dS = C_p\,dT + T\left.\frac{\partial S}{\partial p}\right|_T \left(\left.\frac{\partial p}{\partial T}\right|_V dT + \left.\frac{\partial p}{\partial V}\right|_T dV\right) \tag{4.138}$$

Since dS is a complete differential, the coefficients of dT in Equations (4.136) and (4.138) have to be equal, i.e.,

$$C_V = C_p + T\left.\frac{\partial S}{\partial p}\right|_T \left.\frac{\partial p}{\partial T}\right|_V \tag{4.139}$$

By the way, this is also the case for the coefficient of dV. This is proved via the chain rule $\left.\frac{\partial S}{\partial p}\right|_T \left.\frac{\partial p}{\partial V}\right|_T = \left.\frac{\partial S}{\partial V}\right|_T$. Equation (4.139) for the relationship between C_V and C_p is, however, still not very useful in practice, since for instance $\partial S/\partial p|_T$ is difficult to measure. The quantity $\partial p/\partial T|_V$ is conveniently measurable for gases, but in fluids or solids processes at constant volume are connected with extreme pressure. Thus, if possible, we want to express both quantities in terms of easily measurable quantities. The Maxwell relation (4.133) reads

$$\left.\frac{\partial S}{\partial p}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_p \tag{4.140}$$

The righthand side is the isobaric expansion coefficient α,

$$\left.\frac{\partial V}{\partial T}\right|_p = \alpha V \tag{4.141}$$

Also, the factor $\partial p/\partial T|_V$ can be rewritten with an often used trick in terms of other quantities. To this end, we consider the volume as a function of p and T, since these variables determine the state of the system as well as V and T; then we have

$$dV = \left.\frac{\partial V}{\partial T}\right|_p dT + \left.\frac{\partial V}{\partial p}\right|_T dp$$

For processes at constant volume ($dV = 0$) it thus holds that

$$\left.\frac{\partial p}{\partial T}\right|_V = -\frac{\left.\frac{\partial V}{\partial T}\right|_p}{\left.\frac{\partial V}{\partial p}\right|_T} \tag{4.142}$$

In the numerator we have the expansion coefficient αV, while in the denominator the isothermal compressibility κV appears:

$$\left.\frac{\partial V}{\partial p}\right|_T = -V\kappa \tag{4.143}$$

If one inserts Equations (4.140–4.143) into Equation (4.139), it finally follows that

$$C_p = C_V + TV\frac{\alpha^2}{\kappa}$$

In this relation only quantities which are easy to determine appear.

Example 4.13: Joule–Thomson experiment

From daily experience we know that a container filled with gas under large pressure cools down when the gas escapes (e.g., for sprays). Since no external work is performed in the expansion ($\delta A = 0$) and since the expansion happens very fast so that no heat is exchanged with the surroundings ($\delta Q = 0$), this process is an irreversible adiabatic expansion of a real gas. Since $\delta A = 0$ and $\delta Q = 0$ we also have $dU = 0$. For an ideal gas or a van der Waals gas we can determine the change of the temperature. For the latter case we have already calculated the internal energy $U(V, T)$ in Equation (3.62):

$$U(V, T) = U_0(V_0, T_0) + C_V(T - T_0) - N^2 a\left(\frac{1}{V} - \frac{1}{V_0}\right)$$

For an ideal gas we simply put $a = 0$. With $\Delta U = 0$ it follows that

$$\Delta T = \frac{N^2 a}{C_V}\left(\frac{1}{V} - \frac{1}{V_0}\right).$$

The maximum change of temperature ΔT for the expansion into a very large volume ($V \to \infty$) is

$$\Delta T = -\frac{N^2 a}{C_V V_0}$$

For ideal gases we thus have $\Delta T = 0$, while for real van der Waals gases ($a > 0$) the temperature change is negative. The reason is that in the expansion internal work is performed against the molecular attractive forces, the strength of which is measured via the constant a. We want to investigate the irreversible expansion of an arbitrary real gas in somewhat more detail. To have definite thermodynamic conditions at every moment of the expansion one needs a device which slows down the spontaneous and thus irreversible expansion of the gas, so that one has a certain well-defined pressure at each moment. One achieves this via a porous plug (throttle), which permits only a small amount of gas to pass at each moment. Simultaneously the pressures on both sides of the throttle are continuously kept constant.

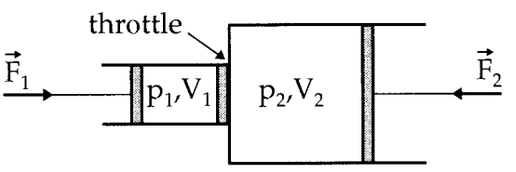


Figure 4.9. Joule–Thomson experiment.

A possible practical set-up is shown in Figure 4.9. Pistons 1 and 2 (in practice the role of the pistons is assumed by a pump) provide at each moment a steady flood of gas from pressure p_1 to the smaller pressure p_2, whereby the volume V_2 increases. We must now isolate the whole set–up well to provide adiabacity ($\delta Q = 0$). We consider a certain amount of gas which has the volume V_1 at pressure p_1 and which is pumped to the other side of the throttle where it then takes the volume V_2 at pressure p_2. The change of the internal energy of this amount of gas is given by the work done on the left side to expell the gas at constant pressure p_1 from volume V_1, which is $p_1 V_1$ minus the work which is performed by the gas at constant pressure p_2 against piston 2, so that the gas takes the volume V_2, which

is p_2V_2.

$$U_2 - U_1 = p_1V_1 - p_2V_2$$

or

$$U_1 + p_1V_1 = U_2 + p_2V_2$$

The enthalpy $U + pV$ remains constant on both sides; one says that the process happens isenthalpically. We now want to calculate for a given pressure change dp the change in temperature dT at constant enthalpy. To this end we assume H to be a function of T and p:

$$dH = \left.\frac{\partial H}{\partial T}\right|_p dT + \left.\frac{\partial H}{\partial p}\right|_T dp$$

For $H = \text{const.}$ we have $dH = 0$, and thus the temperature change under a change of pressure is

$$\left.\frac{\partial T}{\partial p}\right|_H = -\frac{\left.\frac{\partial H}{\partial p}\right|_T}{\left.\frac{\partial H}{\partial T}\right|_p}$$

Here we have simply $\partial H/\partial T|_p = C_p$. We also want to express $\partial H/\partial p|_T$ by simply measurable quantities. With ($N = \text{const.}$):

$$dH = T\,dS + V\,dp$$

we have

$$\left.\frac{\partial H}{\partial p}\right|_T = T\left.\frac{\partial S}{\partial p}\right|_T + V = V - T\left.\frac{\partial V}{\partial T}\right|_p$$

where we have used the Maxwell relation $\partial S/\partial p|_T = -\partial V/\partial T|_p$. Finally the Joule–Thomson coefficient δ is given by

$$\left.\frac{\partial T}{\partial p}\right|_H = \delta = \frac{1}{C_p}\left(T\left.\frac{\partial V}{\partial T}\right|_p - V\right)$$

$$= \frac{V}{C_p}(T\alpha - 1) \qquad \textbf{(4.144)}$$

where $\alpha V = \partial V/\partial T|_p$ is the isobaric expansion coefficient, which for an ideal gas has just the value $\alpha = 1/T$, so that (for an ideal gas) $\delta = 0$. We now want to evaluate Equation (4.144) for special equations of state of real gases. To this end, we use an approximation for van der Waals' equation, since this equation is difficult to solve for V:

$$\left(p + \left(\frac{N}{V}\right)^2 a\right)(V - Nb) = NkT$$

$$\Leftrightarrow V = \frac{NkT}{p} - \frac{N^2a}{pV} + Nb + \left(\frac{N}{V}\right)^2 \frac{Nab}{p}$$

Now we replace V in zeroth approximation by NkT/p on the righthand side. Moreover, we assume we have a fixed amount of gas (1 mole), i.e., $N = N_A$ and $Nk = R$. The constants a and b shall refer to 1 mole; i.e., we put $N_A^2a \to a$ and $N_Ab \to b$. Then V is equal to the

molar volume v for which we obtain in a first successive approximation,

$$v = \frac{RT}{p} - \frac{a}{RT} + b + \frac{abp}{R^2T^2}$$

From this we can calculate the required derivative,

$$T \left.\frac{\partial v}{\partial T}\right|_p = \frac{RT}{p} + \frac{a}{RT} - 2\frac{abp}{R^2T^2}$$

The difference $T \left.\frac{\partial v}{\partial T}\right|_p - v$ can thus be readily given in explicit terms, so that according to Equation (4.144)

$$\delta = \left.\frac{\partial T}{\partial p}\right|_H = \frac{1}{C_p}\left(\frac{2a}{RT} - b - 3\frac{abp}{R^2T^2}\right) \qquad \textbf{(4.145)}$$

For nitrogen, for instance, we have $a = 0.141\ \mathrm{m^6\,Pa\,mol^{-2}}$ and $b = 0.03913 \cdot 10^{-3}\ \mathrm{m^3\,mol^{-1}}$. At room temperature and a pressure $p = 10^7$ Pa Equation (4.145) yields $\delta_{\mathrm{theo}} = 0.188°\mathrm{C}/10^5$ Pa, while the measured value is $\delta_{\mathrm{exp}} = 0.141°\mathrm{C}/10^5$ Pa.

Equation (4.145) predicts not only cooling down under expansion ($\delta > 0$), but in certain regions also reheating. One calls the temperature–pressure curve at which δ just vanishes the *inversion curve*. In an expansion gases only cool down, if for a given pressure the initial temperature was smaller than the inversion temperature; in the other case they even heat up. From Equation (4.145) we can calculate the inversion curve:

$$\delta = 0 \Leftrightarrow T_i^2 - \frac{2a}{Rb}T_i + \frac{3ap}{R^2} = 0$$

As one observes, two inversion temperatures exist for each pressure below a certain critical pressure p_{max}. The inversion curve is a parabola in the Tp diagram, which separates the region of cooling from the region of reheating. Also shown in the diagram are the isenthalpics ($H(p, T) = \mathrm{const.}$). The slope of these curves is just the Joule–Thomson coefficient, according to Equation (4.144). The inversion curve connects the maxima of the isenthalpics.

If the relaxation of the gas happens over a wide range of pressures, one has to integrate the Joule–Thomson coefficient δ over the pressure change (here we reverse the substitution $N_A^2 a \to a$ and $N_A b \to b$):

$$\begin{aligned}\Delta T &= \int_{p_0}^{p_1} \left.\frac{\partial T}{\partial p}\right|_H dp \\ &= \int_{p_0}^{p_1} \frac{N}{C_p}\left(\frac{2a}{kT} - b - 3\frac{abp}{(kT)^2}\right) dp\end{aligned}$$

Here T and p, of course, are not independent variables. For each infinitesimal pressure change the temperature also changes in a fixed way. The variables T and p are mutually related via $H(p, T) = \mathrm{const.}$, and the relaxation happens along an isenthalpic in the figure.

The irreversible expansion of real gases has great technical importance for achieving very low temperatures, as well as in the liquefaction of technical gases. It is used, for example, in *Linde's liquefaction process* (Figure 4.11). To use the temperature decrease more efficiently one leads the expanded, cooled gas through a heat exchanger, whereby the highly compressed gas is further cooled down.

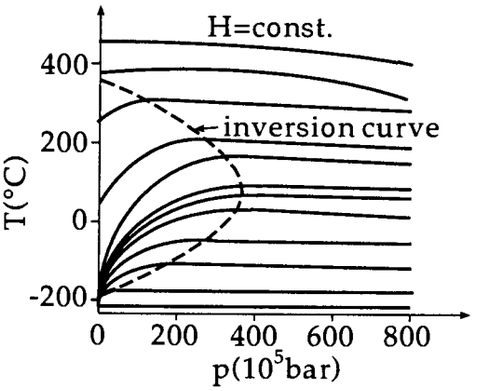


Figure 4.10. Experimental inversion curve and isenthalpics (H = const.) for nitrogen.

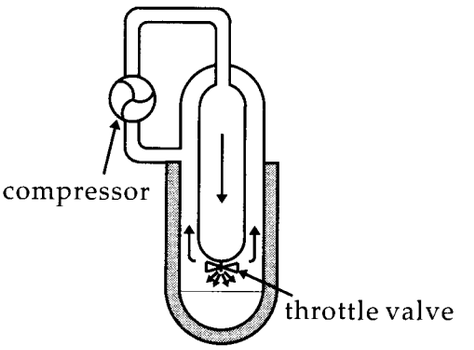


Figure 4.11. Linde's liquefaction process (schematically).

However, this process works only for gases which have an inversion temperature (at a given compressor pressure) above that of room temperature (e.g., air, CO_2, N_2, ...).

For hydrogen precooling is necessary, since the inversion temperature of hydrogen (≈ -80°C) lies below room temperature.

A temperature decrease always happens in the *reversible* expansion of real gases, since the gas has to additionally perform external work. This process, however, is more difficult to realize and is thus of no great technical importance.

Jacobi transformations

A frequently occurring problem in thermodynamics is the transformation of variables in state functions. Such transformations must not be confused with the Legendre transformation. For the latter we have not simply replaced one variable in the internal energy by another, but have defined a new physical quantity, which is especially convenient for a certain system. In the following we want to investigate pure transformations of variables in the same physical quantity.

Example 4.14: Calculation of C_p from the entropy

A nice example illustrating the use of Jacobi transformations is the calculation of derivatives at "wrong" fixed variables. Given the entropy $S(U, V, N)$, calculate

$$C_p = T \left.\frac{\partial S}{\partial T}\right|_p \tag{4.146}$$

Obviously, this case is quite inconvenient, because we need $S(T, p, N)$ instead of $S(U, V, N)$. The question now is whether the derivative $\partial/\partial T|_p$ can be expressed in terms of derivatives

with respect to U and V. First, we consider the complete differential of $S(U, V, N)$,

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN \tag{4.147}$$

From this we obtain

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N}, \qquad \frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N} \tag{4.148}$$

Since for the following considerations we generally have $N = \text{const.}$, we can omit the variable N. Since $S(U, V)$ is known, Equation (4.148) yields the functions $T(U, V)$ and $p(U, V)$, which are thus also known. In principle one could solve these two functions for $U(T, p)$ and $V(T, p)$ and substitute in $S(U, V)$. One would thus obtain $S(T, p)$, but this way is very tedious and even not practicable in general. The following procedure is more clear:

Since $T(U, V)$ and $p(U, V)$ are known from Equation (4.148), we can calculate the total differentials,

$$dT = \left.\frac{\partial T}{\partial V}\right|_U dV + \left.\frac{\partial T}{\partial U}\right|_V dU \tag{4.149}$$

$$dp = \left.\frac{\partial p}{\partial V}\right|_U dV + \left.\frac{\partial p}{\partial U}\right|_V dU \tag{4.150}$$

The coefficients of dV and dU are assumed to be known. The way to calculate Equation (4.146) is the following: one solves Equations (4.149) and (4.150) for dU and dV and replaces these differentials in Equation (4.147) by dT and dp. The coefficient of dT is $\partial S/\partial T|_p$, and that of dp is $\partial S/\partial p|_T$. We want to make this concrete. The solution of the system of Equations (4.149) and (4.150) is most simply performed with the help of the determinant rule. This, however, is only possible if the determinant of the coefficients

$$J(U, V) = \begin{vmatrix} \left.\frac{\partial T}{\partial V}\right|_U & \left.\frac{\partial T}{\partial U}\right|_V \\ \left.\frac{\partial p}{\partial V}\right|_U & \left.\frac{\partial p}{\partial U}\right|_V \end{vmatrix} = \left.\frac{\partial T}{\partial V}\right|_U \left.\frac{\partial p}{\partial U}\right|_V - \left.\frac{\partial T}{\partial U}\right|_V \left.\frac{\partial p}{\partial V}\right|_U \tag{4.151}$$

does not vanish.

$J(U, V)$ is the *Jacobi determinant* of the transformation $(U, V) \to (T, p)$ and depends here on the old variables. If the determinant in Equation (4.151) vanishes, the transformation from U and V to T and p is not unique. According to the determinant rule we have

$$x_i = \frac{\det_{A_i}}{\det_A} \qquad \text{for} \quad \hat{A}\vec{x} = \vec{b} \text{ and } \det \hat{A} \neq 0, \tag{4.152}$$

where x_i are the unknowns of the system of equations and $\hat{A}_i$ is the coefficient matrix, where the ith column is replaced by the inhomogeneous vector $\vec{b}$. In our case Equation (4.152) reads, with the inhomogeneity (dT, dp),

$$dU = \frac{1}{J(U, V)}\left(-\left.\frac{\partial p}{\partial V}\right|_U dT + \left.\frac{\partial T}{\partial V}\right|_U dp\right) \tag{4.153}$$

$$dV = \frac{1}{J(U, V)}\left(+\left.\frac{\partial p}{\partial U}\right|_V dT - \left.\frac{\partial T}{\partial U}\right|_V dp\right) \tag{4.154}$$

If we insert Equations (4.153) and (4.154) into Equation (4.147), it follows that ($dN = 0$)

$$\begin{aligned} dS = & \frac{1}{TJ(U,V)} \left(-\left.\frac{\partial p}{\partial V}\right|_U dT + \left.\frac{\partial T}{\partial V}\right|_U dp \right) \\ & + \frac{p}{TJ(U,V)} \left(+ \left.\frac{\partial p}{\partial U}\right|_V dT - \left.\frac{\partial T}{\partial U}\right|_V dp \right) \\ = & \frac{1}{TJ} \left(-\left.\frac{\partial p}{\partial V}\right|_U + p \left.\frac{\partial p}{\partial U}\right|_V \right) dT \\ & + \frac{1}{TJ} \left(-p \left.\frac{\partial T}{\partial U}\right|_V + \left.\frac{\partial T}{\partial V}\right|_U \right) dp \end{aligned}$$

Here one immediately reads off

$$\left.\frac{\partial S}{\partial T}\right|_p = \frac{1}{TJ(U,V)} \left(-\left.\frac{\partial p}{\partial V}\right|_U + p \left.\frac{\partial p}{\partial U}\right|_V \right) \tag{4.155}$$

The quantities $\partial p/\partial V|_U$ und $\partial p/\partial U|_V$ can be explicitly calculated, since $p(U, V)$ is known. However, Equation (4.155) yields the quantity $\partial S/\partial T|_p$ not as a function of the variables T and p, but as a function of the old variables U, V. With the help of the Equations (4.148) one can nevertheless rewrite $\partial p/\partial V|_U$ and $\partial p/\partial U|_V$ in terms of the new variables T and p.

In this example we can already convince ourselves of the usefulness of the concept of the Jacobi determinant. In general, the Jacobi determinant for the transformation from the variables $(x_1, x_2, \ldots, x_n)$ to the new variables $(u_1, u_2, \ldots, u_n)$ is defined by

$$J(x_1, \ldots, x_n) = \begin{vmatrix} \frac{\partial u_1}{\partial x_1} & \frac{\partial u_1}{\partial x_2} & \cdots & \frac{\partial u_1}{\partial x_n} \\ \frac{\partial u_2}{\partial x_1} & \frac{\partial u_2}{\partial x_2} & \cdots & \frac{\partial u_2}{\partial x_n} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial u_n}{\partial x_1} & \frac{\partial u_n}{\partial x_2} & \cdots & \frac{\partial u_n}{\partial x_n} \end{vmatrix} \tag{4.156}$$

It is also denoted as

$$J(x_1, \ldots, x_n) = \frac{\partial(u_1, \ldots, u_n)}{\partial(x_1, \ldots, x_n)} \tag{4.157}$$

According to the rules for multiplication of determinants

$$\frac{\partial(u_1, \ldots, u_n)}{\partial(w_1, \ldots, w_n)} \frac{\partial(w_1, \ldots, w_n)}{\partial(x_1, \ldots, x_n)} = \frac{\partial(u_1, \ldots, u_n)}{\partial(x_1, \ldots, x_n)} \tag{4.158}$$

This is nothing but a generalized chain rule. For $n = 1$ Equation(4.158) simply reads

$$\frac{du}{dw}\frac{dw}{dx} = \frac{du}{dx} \tag{4.159}$$

Exchange of columns or rows in the Jacobi determinant yields a minus sign. Because of Equation (4.158) the Jacobi determinant of the reverse transformation

$$\frac{\partial(x_1, \ldots, x_n)}{\partial(u_1, \ldots, u_n)} = \left(\frac{\partial(u_1, \ldots, u_n)}{\partial(x_1, \ldots, x_n)}\right)^{-1} \tag{4.160}$$

is just the inverse of the original transformation.

Especially useful is the denotation of a derivative as a Jacobi determinant,

$$\left.\frac{\partial u}{\partial x_1}\right|_{x_2, x_3, \ldots, x_n} = \frac{\partial(u, x_2, \ldots, x_n)}{\partial(x_1, x_2, \ldots, x_n)} = \begin{vmatrix} \frac{\partial u}{\partial x_1} & & & 0 \\ & 1 & & \\ & & \ddots & \\ 0 & & & 1 \end{vmatrix} \tag{4.161}$$

since u can only depend on x_1.

Example 4.15: Joule–Thomson coefficient

While discussing the Joule–Thomson experiment we calculated the Joule–Thomson coefficient

$$\delta = \left.\frac{\partial T}{\partial p}\right|_H$$

If δ is to be expressed by the known enthalpy $H(T, p)$, one obtains this with the help of

$$\left.\frac{\partial T}{\partial p}\right|_H = \frac{\partial(T, H)}{\partial(p, H)} = \frac{\partial(T, H)}{\partial(p, T)}\frac{\partial(p, T)}{\partial(p, H)} = \frac{\partial(T, H)}{\partial(p, T)} \Big/ \frac{\partial(p, H)}{\partial(p, T)}$$

or

$$\left.\frac{\partial T}{\partial p}\right|_H = -\frac{\partial(H, T)}{\partial(p, T)} \Big/ \frac{\partial(p, H)}{\partial(p, T)} = -\left.\frac{\partial H}{\partial p}\right|_T \Big/ \left.\frac{\partial H}{\partial T}\right|_p$$

which, of course, agrees with the result above.

Thermodynamic stability

We have seen in the preceding sections that the thermodynamic *equilibrium states* are characterized by a maximum of the entropy, or by a minimum in the various thermodynamic

potentials, respectively. Then one can immediately derive some relations, the so-called conditions for thermodynamic stability, which can be directly determined from the second derivative of the potentials.

For instance, for the isothermal compressibility it must hold that:

$$\kappa = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_T \geq 0 \tag{4.162}$$

This means that in equilibrium a spontaneous decrease of the volume ($\partial V < 0$) effects an increase of the pressure ($\partial p > 0$), so that the system moves by itself back towards the equilibrium state.

Similarly the heat capacities must be C_p, $C_V \geq 0$, so that a spontaneous temperature increase—which would correspond to an energy increase—cannot happen. These two conditions are special requirements which follow from the *Braun–Le Chatelier principle*:

> If a system is in stable equilibrium, then *all* spontaneous changes of the parameters must invoke processes which bring the system back to equilibrium, i.e., which work against these spontaneous changes.

PART II

STATISTICAL MECHANICS

5 Number of Microstates Ω and Entropy S

Foundations

Up to now, we have described the macroscopic properties of matter phenomenologically with the aid of equations of state which had been derived empirically. For thermodynamics it is of no importance, in this connection, how a certain equation of state comes about. On the one hand, this is the reason for the large universality of thermodynamics; on the other hand, however, from the point of view of physical insight, it is a little unsatisfactory. We have already seen that many quantities of state (temperature, entropy) and equations of state (ideal gas, van der Waals gas) can be very well understood with the aid of microscopic considerations.

The macroscopic quantities of state result from taking mean values of microscopic properties. For example, the pressure of a gas is due to the collisions of the molecules with a surface, whereas temperature is directly given by the mean kinetic energy of the particles.

It is now the task of statistical mechanics to define in an exact way the process of taking mean values, which leads from the microscopic quantities (momenta, coordinates) to the macroscopic quantities of state, thus providing a connection between the atomistic, microscopic theory of matter and macroscopic thermodynamics. The key to this connection is entropy (as already emphasized in Chapter 2), which has a very simple and immediately understandable microscopic interpretation: we have already connected the entropy uniquely to the number of possible microstates Ω in a given macrostate (U, V, N), $S \propto \ln \Omega$. This relation provides the basic connection between macroscopic thermodynamics (entropy) and statistical microscopic physics (number of states).

Now we will first make the notion *number of microstates* more precise, and then we will give a prescription on how to calculate it. Already, with a few requirements, it will be possible to calculate equations of state for some concrete physical systems microscopically.

The essential superiority of statistical mechanics, however, will not become apparent until the modern formulation of *ensemble* theory. There the macroscopic quantities are defined as mean values of microscopic quantities, weighted with probability densities.

Phase space

First we want to examine in more detail what has to be understood under the notion *microstate*. For a *classical* system it is sufficient to know at a time t all generalized coordinates $q_\nu(t)$ and momenta $p_\nu(t)$ to uniquely fix the state of motion of the system. Thus for a mechanical system we can interpret the set (q_ν, p_ν), $\nu = 1, \ldots, 3N$ as the microstate of this system, where for simplicity we enumerate coordinates and momenta from 1 to $3N$, as long as there are no constraints for coordinates or momenta. The set (q_ν, p_ν) can now be understood as a point in a $6N$-dimensional space which is called the classical *phase space*.

A definite point in this phase space exactly corresponds to one microscopic state of motion of the whole system. Analogously, one can relate to each particle a 6-dimensional phase space (one-particle phase space). The state of motion of the system is then described by N points in this one-particle phase space. If not explicitly stated differently, however, we always want to understand as phase space the high dimensional space of the whole system.

The temporal evolution of the system corresponds to one curve $(q_\nu(t), p_\nu(t))$ in phase space, which is called the *phase-space trajectory*. It is determined by Hamilton's equations of motion

$$\dot{q}_\nu = \frac{\partial H}{\partial p_\nu}, \qquad \dot{p}_\nu = -\frac{\partial H}{\partial q_\nu} \tag{5.1}$$

The Hamiltonian $H(q_\nu(t), p_\nu(t))$ corresponds to the (possibly time-dependent) total energy of the system. It is a function of the phase-space point (q_ν, p_ν) and of time, and according to Equation (5.1) it determines the temporal evolution of the system. In a closed global system, in which the Hamiltonian does not depend explicitly on time, the total energy

$$E = H(q_\nu(t), p_\nu(t)) \tag{5.2}$$

is a conserved quantity, which along the phase-space trajectory $(q_\nu(t), p_\nu(t))$ always assumes the same time-independent value, E. In general, the time dependence of an observable quantity $A(q_\nu(t), p_\nu(t), t)$ is given by

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \sum_{\nu=1}^{3N} \left(\frac{\partial A}{\partial q_\nu} \dot{q}_\nu + \frac{\partial A}{\partial p_\nu} \dot{p}_\nu \right) \tag{5.3}$$

which, using Equation (5.1), can be rewritten as:

$$\begin{aligned} \frac{dA}{dt} &= \frac{\partial A}{\partial t} + \sum_{\nu=1}^{3N} \left(\frac{\partial A}{\partial q_\nu} \frac{\partial H}{\partial p_\nu} - \frac{\partial A}{\partial p_\nu} \frac{\partial H}{\partial q_\nu} \right) \\ &= \frac{\partial A}{\partial t} + \{A, H\} \end{aligned} \tag{5.4}$$

Here we have used the *Poisson bracket* $\{A, H\}$ as an abbreviation for the sum. Especially for $A = H$ with $\partial H/\partial t = 0$ and $\{H, H\} = 0$ we just recover the conservation of energy. Equation (5.4) describes a $(6N-1)$-*dimensional hypersurface in phase space*. For a particle which moves in only one dimension we can easily elucidate the introduced notions.

Example 5.1: Harmonic oscillator

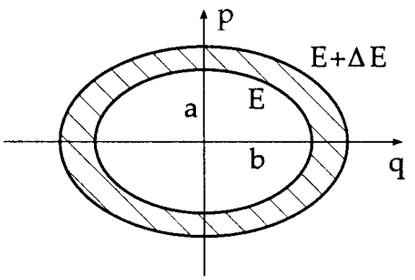


Figure 5.1. Phase space of the one-dimensional harmonic oscillator.

The Hamiltonian of a harmonic oscillator in one dimension reads

$$H(q, p) = \frac{p^2}{2m} + \frac{1}{2} K q^2 \tag{5.5}$$

if m is the mass of the particle and K is the oscillator constant. To Equation (5.5) there corresponds a two-dimensional phase space, as shown in Figure 5.1. Since H does not explicitly depend on time—we assume this in the following—the total energy is a conserved quantity. The energy hypersurface

$$H(q, p) = \frac{p^2}{2m} + \frac{1}{2} K q^2 = \text{const.}$$

is just an ellipse in one-particle phase space which is determined by the value of E. The half-axes are $a = \sqrt{2mE}$ and $b = \sqrt{2E/K}$. With the given frequency $\omega = \sqrt{K/m}$, the surface of the ellipse becomes $\sigma = \pi ab = 2\pi E/\omega$. During its temporal evolution the actual phase-space point $(q(t), p(t))$ of the system can move only on this ellipse. In the figure we have drawn two such ellipses which differ only slightly in energy. Each point on the ellipses corresponds to a concrete state of motion (snapshot) of the oscillator with an energy between E and $E + \Delta E$ at a given moment. Each such phase-space point, however, can be identified with a copy of the actual oscillator in a certain state of motion. This means that the hypersurface also reflects the phase-space distribution of many equal systems at *one* moment. A collection of such phase-space points (systems) which are consistent with certain macroscopic properties (here: total energy between E and $E + \Delta E$) is called an *ensemble*. In principle, there is of course a continuity of phase-space points, also on one energy surface, but as an illustration one often selects a (finite) number of representative phase-space points.

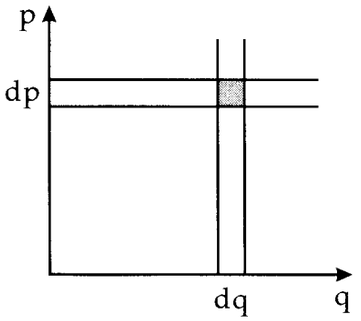


Figure 5.2. Subdivision of phase space.

In analogy to the usual three-dimensional space, one can also subdivide a high dimensional phase space into volume elements $d^{3N}q\, d^{3N}p$. For a two-dimensional phase space (one coordinate, one momentum) this is illustrated in Figure 5.2.

The phase-space element $d^{3N}q\, d^{3N}p$, which can be of finite size, is called a *phase-space cell*. Hence we are able to relate volumes to certain regions of phase space (e.g., between the ellipses E, $E + \Delta E$).

In general, phase-space volumes shall be abbreviated with the letter ω (which must not be confused with frequencies). Consequently, the shorthand notation of a phase-space cell $d^{3N}q\, d^{3N}p$ is $d\omega$. For example, for the phase-space volume between the ellipses corresponding to E and $E + \Delta E$, respectively, we have

$$\Delta\omega = \int_{E \le H(q,p) \le E+\Delta E} dq\, dp = \int_{E \le H(q,p) \le E+\Delta E} d\omega \tag{5.6}$$

In the same way, according to Equation (5.2), we can relate an area

$$\sigma(E) = \int_{E=H(q,p)} d\sigma \tag{5.7}$$

to the *energy hypersurface*, where $d\sigma$ denotes the surface element. In the case of Example 5.1 the notion energy *surface* must not be taken too literally, since here the area corresponds to the one-dimensional circumference of the ellipse.

Let us now consider a closed system, which, according to thermodynamics, can be characterized by the natural variables of state E, V, and N. The given container volume in this case restricts the possible coordinates of the particles, because while the total energy is given, only phase-space points on the energy surface are allowed. Nevertheless, for the given macrostate there are a large number $\Omega(E, V, N)$ of different microstates which are consistent with this macrostate. Strictly speaking, there are even an infinite number of them, since the phase-space points in the thermodynamic limit ($V, N \to \infty$) are arbitrarily dense. However, as a measure of the number of microstates, we can use the area of the energy surface, which is at our disposal, and assume $\Omega(E, V, N)$ to be proportional to this surface,

$$\Omega(E, V, N) = \frac{\sigma(E, V, N)}{\sigma_0} \quad \text{with} \quad \sigma(E, V, N) = \int_{E=H(q_\nu, p_\nu)} d\sigma \tag{5.8}$$

where σ_0^{-1} is the constant of proportionality. We will soon see that the essential thermodynamic properties of a system do not depend on the constant σ_0, since we need only the ratios Ω_1/Ω_2 between different macroscopic states (1, 2). This corresponds to the fact that in thermodynamics there appear only differences between thermodynamic potentials, and no absolute values.

The direct calculation of Ω according to Equation (5.8), however, is in most cases very inconvenient, since an integration over a complicated surface in a very high dimensional space is required. In most cases, the calculation of volumes in such spaces is easier. But, according to *Cavalieri's theorem*, this is sufficient for the calculation of the area:

Let $\omega(E, V, N)$ be the total phase-space volume, the boundary of which is given by the energy hypersurface $E = H(q_\nu, p_\nu)$ and the walls of the container in coordinate space. Then we have

$$\omega(E, V, N) = \int_{H(q_\nu, p_\nu) \le E} d^{3N}q\, d^{3N}p \tag{5.9}$$

For small ΔE, the volume between two energy surfaces with energies E and $E + \Delta E$ is given by

$$\Delta\omega = \omega(E + \Delta E) - \omega(E) = \left.\frac{\partial\omega}{\partial E}\right|_{V,N} \Delta E \tag{5.10}$$

On the other hand, according to Cavalieri's theorem, the volume between two neighboring surfaces with area $\sigma(E)$ and distance ΔE is given by

$$\Delta\omega = \sigma(E)\Delta E \tag{5.11}$$

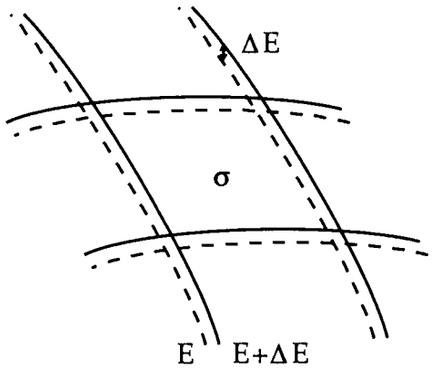


Figure 5.3. Concerning Cavalieri's theorem.

which by comparison with Equation (5.10) gives

$$\sigma(E) = \frac{\partial \omega}{\partial E} \tag{5.12}$$

Equation (5.12) can most easily be made clear with the example of a sphere in the case of three dimensions (Figure 5.3). The volume up to the radius R is $\omega(R) = \frac{4\pi}{3} R^3$. This results in a surface area of $\sigma(R) = \partial\omega/\partial R = 4\pi R^2$. Thus in Equation (5.8) we can calculate

$$\Omega(E, V, N) = \frac{\sigma(E, V, N)}{\sigma_0} = \frac{1}{\sigma_0} \frac{\partial \omega}{\partial E} \tag{5.13}$$

where ω is given by Equation (5.9).

Statistical definition of entropy

As we have already seen in Chapter 2, in thermodynamic equilibrium the most probable macroscopic state is the one which corresponds to the largest number of consistent microstates. Here enters the basic postulate that all microstates with the same total energy appear with the same probability.

Let us consider a closed system which consists of two subsystems with the variables of state E_i, V_i, and N_i, $i = 1, 2$, so that

$$\begin{aligned} E &= E_1 + E_2 = \text{const.} & dE_1 &= -dE_2 \\ V &= V_1 + V_2 = \text{const.} & dV_1 &= -dV_2 \\ N &= N_1 + N_2 = \text{const.} & dN_1 &= -dN_2 \end{aligned} \tag{5.14}$$

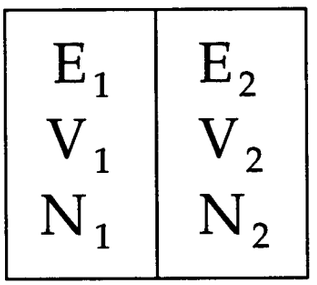


Figure 5.4. System of two subsystems.

i.e., the partial systems may exchange energy or particles, or they may change their volume. However, in equilibrium E_i, V_i, and N_i will adapt to certain mean values. Now the total number of all microstates of the total system $\Omega(E, V, N)$ results as the product of these numbers for the subsystems, if the latter can be considered to be statistically independent:

$$\Omega(E, V, N) = \Omega_1(E_1, V_1, N_1)\Omega_2(E_2, V_2, N_2) \tag{5.15}$$

The most probable state, i.e., the equilibrium state, is the one with the largest number of microstates, i.e., $\Omega = \Omega_{\max}$ and $d\Omega = 0$. If we form the total differential of Equation (5.15) we get

$$d\Omega = \Omega_2\, d\Omega_1 + \Omega_1\, d\Omega_2 \tag{5.16}$$

or, dividing by Equation (5.15),

$$d \ln \Omega = d \ln \Omega_1 + d \ln \Omega_2 \tag{5.17}$$

The equilibrium condition reads

$$d \ln \Omega = 0 \qquad \ln \Omega = \ln \Omega_{\max} \tag{5.18}$$

Considering the same system from a purely thermodynamic point of view, when the internal energy U of a closed system is identified with the total energy E the entropy is given by

$$S(E, V, N) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \tag{5.19}$$

The total differential is

$$dS = dS_1 + dS_2 \tag{5.20}$$

We are in equilibrium exactly if the entropy is maximal:

$$dS = 0 \qquad S = S_{\max} \tag{5.21}$$

Comparison of Equation (5.17) with Equation (5.20), and Equation (5.18) with Equation (5.21) reveals the complete analogy of ln Ω and entropy. Both quantities therefore must be proportional to each other, and we define

$$S(E, V, N) = k \ln \Omega(E, V, N) \tag{5.22}$$

where k is a constant with the dimension of an entropy. In the following example we will identify it as Boltzmann's constant.

Remark: In general, we would have

$$S = k \ln \Omega(E, V, N) + \text{const.} \tag{5.23}$$

However, since S is only defined up to a constant, the constant can be absorbed in S.

Equation (5.22) is of fundamental significance for statistical mechanics. It allows one, at least in principle, to calculate all thermodynamic properties of a given many-body system using the Hamiltonian $H(p_\nu, q_\nu)$. This is so because the knowledge of the thermodynamic potential $S(E, V, N)$ as a function of the natural variables at the same time gives us the equations of state via

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N}, \qquad \frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N}, \qquad -\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_{E,V} \tag{5.24}$$

Unfortunately, the practical calculation of Ω is by no means trivial, and only the general ensemble theory, which we will treat in subsequent sections, will give us a practicable method for the calculation of more complicated systems. Equation (5.24) also shows why the constant of proportionality σ_0 of Equation (5.8) has no practical consequences. It gives an additive contribution to entropy, but in thermodynamics only entropy differences are measured.

Nevertheless, this constant σ_0 deserves still more detailed consideration. In principle, it has the significance of a surface element on the energy surface assumed by a microstate. In classical considerations this does not make very much sense, since the microstates are arbitrarily dense and thus one uses an arbitrary unit surface. In quantum mechanics, however, because of the uncertainty relation, each microstate occupies at least a volume $\Delta p\, \Delta q \geq h$,

or $\Delta^{3N}p\,\Delta^{3N}q \geq h^{3N}$. Now the constant σ_0 acquires physical significance! The quantum mechanical phase space consists of cells of magnitude h^{3N}. These cells have a finite volume, and it makes sense to count the microstates absolutely. So we see that quantum mechanically it is possible to identify Ω with the discrete numbers of microstates, which are fixed by the quantum numbers. In this case, Equation (5.22) gives the absolute entropy without an additive constant. The entropy $S = 0$ then corresponds to a system which can assume only one exactly defined microstate ($\Omega = 1$). In practice, such systems are, for instance, ideal crystals at the temperature $T = 0$. The statement that such systems at $T = 0$ have the entropy $S = 0$ is also called *the third law of thermodynamics.*

Now we want to demonstrate the practical calculation which is necessary for the evaluation of Equation (5.22) for the ideal gas.

Example 5.2: Statistical calculation of the entropy of the ideal gas

The Hamiltonian of the ideal gas reads

$$H(q_\nu, p_\nu) = \sum_{\nu=1}^{N} \frac{\vec{p}_\nu^{\,2}}{2m} = \sum_{\nu=1}^{3N} \frac{p_\nu^2}{2m} \tag{5.25}$$

where, for simplicity we have numbered the coordinates and momenta from 1 to $3N$. First, we evaluate $\omega(E, V, N)$ according to Equation (5.9):

$$\omega(E, V, N) = \int_{H(p_\nu, q_\nu)\leq E} d^{3N}q\, d^{3N}p$$

Since the Hamiltonian of the ideal gas does not depend on the coordinates of the particles, the integral over the coordinates can be calculated immediately:

$$\omega(E, V, N) = V^N \int_{H(p_\nu)\leq E} d^{3N}p \tag{5.26}$$

The remaining integral is just the volume of a $3N$-dimensional sphere of radius $\sqrt{2mE}$, since the condition $H(p_\nu) \leq E$ explicitly reads

$$\sum_{\nu=1}^{3N} p_\nu^2 \leq (\sqrt{2mE})^2$$

This condition is met by all points of momentum space which lie in the interior of a sphere with radius $\sqrt{2mE}$. Therefore, we want to start by calculating in general the volume $V_N(R)$ of an N-dimensional sphere with the radius R. We have

$$V_N(R) = \int_{\sum_{i=1}^{3N} x_i^2 \leq R^2} dx_1 \cdots dx_N = R^N \int_{\sum_{i=1}^{3N} y_i^2 \leq 1} dy_1 \cdots dy_N$$

Here we have substituted $y_i = x_i/R$ as a new variable. The last integral no longer depends on R but only on the dimension N of space:

$$V_N(R) = R^N C_N$$

$$C_N = \int_{\sum_{i=1}^{3N} y_i^2 \leq 1} dy_1 \cdots dy_N$$

where C_N is just the volume of the N-dimensional unit sphere. To calculate this we use a trick. It is well known that

$$\int_{-\infty}^{+\infty} dx \exp\{-x^2\} = \sqrt{\pi}$$

and thus

$$\int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_N \exp\{-(x_1^2 + \cdots + x_N^2)\} = \pi^{N/2} \tag{5.27}$$

Now the integrand of Equation (5.26) depends only on $R = (x_1^2 + \cdots + x_N^2)^{1/2}$, and we can thus express the volume element $dx_1 \cdots dx_N$ by spherical shells, using Equation (5.25):

$$\begin{aligned} dx_1 \cdots dx_N|_{\text{shell}} &= dV_N(R)|_{\text{shell}} \\ &= NR^{N-1}C_N\, dR \end{aligned}$$

This corresponds to a transformation to polar coordinates in N-dimensional space. Then Equation (5.26) is equivalent to

$$NC_N \int_0^{\infty} R^{N-1}\, dR \exp\{-R^2\} = \pi^{N/2}$$

Using this we can easily calculate C_N, because with the substitution $R^2 = x$ the integral just gives the Γ-function,

$$NC_N \frac{1}{2} \int_0^{\infty} dx x^{N/2-1} e^{-x} = \pi^{N/2} \tag{5.28}$$

As per definition, the Γ-function is

$$\Gamma(z) = \int_0^{\infty} dx x^{z-1} e^{-x} \tag{5.29}$$

So we have calculated C_N, the volume of the N-dimensional unit sphere:

$$C_N = \frac{\pi^{N/2}}{\frac{N}{2}\Gamma\left(\frac{N}{2}\right)} \tag{5.30}$$

Especially for $N = 3$, Equations (5.25) and (5.27), with the recursion formula for the Γ-function

$$\Gamma(z+1) = z\Gamma(z) \tag{5.31}$$

and $\Gamma(1/2) = \sqrt{\pi}$, i.e., $\Gamma(3/2) = \frac{1}{2}\sqrt{\pi}$, give

$$V_3(R) = \frac{\pi^{3/2}}{\frac{3}{2}\,\frac{1}{2}\sqrt{\pi}} R^3 = \frac{4\pi}{3} R^3$$

which is just the volume of a 3-dimensional sphere. Correspondingly, the volume of an N-dimensional sphere is given by

$$V_N(R) = \frac{\pi^{N/2}}{\frac{N}{2}\Gamma\left(\frac{N}{2}\right)} R^N$$

For $\omega(E, V, N)$ this gives, according to Equation (5.26) ($3N$ dimensions),

$$\omega(E, V, N) = \frac{\pi^{3N/2}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)} (2mE)^{3N/2} V^N \tag{5.32}$$

Using Equation (5.13) we get

$$\Omega(E, V, N) = \frac{1}{\sigma_0}\frac{\partial \omega}{\partial E} = \frac{1}{\sigma_0} V^N \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} (2m)^{3N/2} E^{3N/2-1} \tag{5.33}$$

so that the entropy of the ideal gas is

$$S(E, V, N) = k \ln \left\{ \frac{1}{\sigma_0} V^N \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} (2m)^{3N/2} E^{3N/2-1} \right\} \tag{5.34}$$

The argument of the logarithm must, of course, be dimensionless. This is indeed the case, since we have

$$\dim\left(\frac{1}{\sigma_0} V^N (2mE)^{3N/2} \frac{1}{E}\right) = \dim\left(\frac{q^{3N} p^{3N}}{\sigma_0 E}\right) = 1$$

because $\sigma_0 E$ has the dimension of a phase-space volume $q^{3N} p^{3N}$ (see, e.g., Equation (5.11)). Equation (5.34) can be considerably simplified if $N \gg 1$, so that $E^{3N/2-1} \approx E^{3N/2}$, and the logarithm of the Γ-function may be approximated according to Stirling's formula:

$$\ln \Gamma(n) \approx (n-1)\ln(n-1) - (n-1) \approx n \ln n - n$$

With the new constant $\sigma = \sigma_0^{1/N}$, the entropy of the ideal gas becomes

$$S(E, V, N) = Nk\left[\frac{3}{2} + \ln\left\{\frac{V}{\sigma}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right\}\right] \tag{5.35}$$

Now we can confirm first that the entropy, Equation (5.35), gives the right equations of state of the ideal gas, and second that the constant k is Boltzmann's constant:

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{3}{2} Nk \frac{1}{E} \quad \text{or} \quad E = \frac{3}{2} NkT \tag{5.36}$$

$$\frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{Nk}{V} \quad \text{or} \quad pV = NkT$$

is valid, independent of σ_0.

Nevertheless, this entropy is not yet the correct entropy of an ideal gas. This can already be seen by the fact that S, according to Equation (5.35), is not a purely extensive quantity. If this were true, the argument of the logarithm would have to depend on intensive quantities only, because in the case of an enlargement of the system by a factor α each extensive factor in the logarithm causes the total entropy to be magnified by a factor α, and in addition a quantity $\ln \alpha$ appears.

Since, however, the calculation is formally correct, obviously there must still be a principal error in the calculation of the entropy. We want to clarify this problem by means of the well-known Gibbs paradox.

Gibbs' paradox

The entropy (5.35) of an ideal gas derived in the preceding example immediately leads to a contradiction which we now want to analyze in more detail. First, with the aid of Equations (5.35) and (5.36) we can calculate the entropy as a function of T, V, and N

$$S(T, V, N) = Nk\left[\frac{3}{2} + \ln\left\{\frac{V}{\sigma}(2\pi mkT)^{3/2}\right\}\right] \tag{5.37}$$

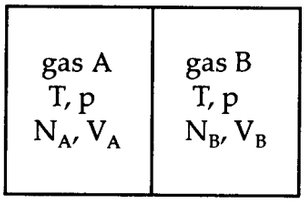


Figure 5.5. Concerning Gibbs' paradox.

Now we consider a closed system consisting of two containers which are separated by a wall and which contain two different ideal gases A and B under the same pressure and at the same temperature (Figure 5.5). If the wall is removed, both gases will spread out over the whole of the container until a new equilibrium situation is reached.

Since the internal energy of ideal gases does not depend on the volume but only on temperature, and since the internal energy remains constant during the whole process, the temperature and pressure do not change either. The entropy, however, increases by a certain value. This so-called *mixing entropy* can be easily calculated using Equation (5.37). Before the removal of the separating wall we have

$$S^{(0)}_{\text{total}} = S^{(0)}_A(T, V_A, N_A) + S^{(0)}_B(T, V_B, N_B) \tag{5.38}$$

and afterwards we have

$$S^{(1)}_{\text{total}} = S^{(1)}_A(T, V_A + V_B, N_A) + S^{(1)}_B(T, V_A + V_B, N_B) \tag{5.39}$$

If here Equation (5.37) is inserted, the entropy difference becomes

$$\Delta S = S^{(1)}_{\text{total}} - S^{(0)}_{\text{total}} = N_A k \ln\left\{\frac{V_A + V_B}{V_A}\right\} + N_B k \ln\left\{\frac{V_A + V_B}{V_B}\right\} \tag{5.40}$$

So far everything seems to be all right, since $\Delta S > 0$, as it should be for this irreversible process.

However, instead of two different gases we can undergo the same considerations for two identical gases. The initial entropy Equation (5.38) is still right, while now, in the final situation, we have

$$S^{(1)}_{\text{total}} = S(T, V_A + V_B, N_A + N_B) \tag{5.41}$$

since now $N_A + N_B$ particles of the same gas are distributed over the total volume $V_A + V_B$. So in this case we receive exactly the same entropy difference $\Delta S > 0$ (Equation (5.40)), as one can easily see by inserting Equation (5.37). However, this cannot be correct, since after the removal of the separating wall in the case of identical gases no macroscopically observable process happens at all. Without any change we can bring in the separating wall again and recover the initial situation. Thus, in the case of identical gases the removal of the separating wall is a reversible process and we must have $\Delta S = 0$.

A more detailed analysis reveals the problem. In classical mechanics the particles are distinguishable: one can enumerate them. Thus for instance, before the removal of the separating wall there are the particles in the left part with certain numbers, e.g., $(1, \ldots, N_A)$, while in the right part (in the case of continual numbering) there are the particles $(N_A + 1, N_A + 2, \ldots, N_A + N_B)$. Now if the wall is removed, the particles, which are here treated like microscopic billiard balls move out over the whole container, and this is indeed an irreversible process, because after the reconstituation of the separating wall, there are particles with different numbers in either compartment. One can mix the particles as long as one likes, one will never (in the case of finite particle number, nearly never) recover the initial situation.

Quantum mechanically, however, this argument does not work. It is in principle impossible to attach to an atom (molecule) a mark (number). The atoms are completely *indistinguishable*. Obviously it is the fact that classical particles are in principle distinguishable (i.e., one can enumerate them), which leads to *Gibbs' paradox*. Hence, if we count the microstates $\Omega(E, V, N)$ of a given macrostate (E, V, N) we must take into account that in reality the particles are not enumerable (distinguishable). In other words, two microstates may only be considered different, if they differ in more than the enumeration of the particles.

In the case of N particles there are exactly $N!$ ways to enumerate them. Therefore, it should be sufficient to reduce the number of microstates just by this factor. Thus, instead of

$$\Omega(E, V, N) = \frac{\sigma(E, V, N)}{\sigma_0} \tag{5.42}$$

we now try a new definition of Ω,

$$\Omega(E, V, N) = \frac{1}{N!} \frac{\sigma(E, V, N)}{\sigma_0} \tag{5.43}$$

where, of course, the calculation of $\sigma(E)$ by $\sigma(E) = \partial\omega/\partial E$ has not been changed.

The factor $1/N!$ in Equation (5.43) is also called the *Gibbs' correction factor*. Its presence proves that classical statistics with distinguishable particles very quickly leads to contradictions with experiment.

Now we want to show that by defining the quantity Ω according to Equation (5.42), Gibbs' paradox is removed. The calculation of $\Omega(E, V, N)$ for an ideal gas in the last example remains unchanged. We must only divide the final results by $N!$; in the case of entropy, we must subtract the term $k \ln N!$. Thus instead of Equation (5.35), we have

$$S(E, V, N) = Nk \left[\frac{3}{2} + \ln \left\{ \frac{V}{\sigma} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right\} \right] - k \ln N!$$

Here for $N \gg 1$ we can also use Stirling's formula ($\ln N! \approx N \ln N - N$), and we get

$$S(E, V, N) = Nk \left[\frac{5}{2} + \ln \left\{ \frac{V}{N\sigma} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right\} \right] \tag{5.44}$$

Entropy is now indeed an extensive quantity, since in the argument of the logarithm there remain only the intensive variables V/N and E/N.

In addition, there also appears the factor $\frac{5}{2}$ (which had already appeared in thermodynamics—see, e.g., Equation (2.81)). If we now calculate the entropy difference in our mixing experiment using Equation (5.44), we obtain

$$S(T, V, N) = Nk\left[\frac{5}{2} + \ln\left\{\frac{V}{N\sigma}(2\pi mkT)^{3/2}\right\}\right] \tag{5.45}$$

because of $E = \frac{3}{2}NkT$. Then according to Equations (5.38) and (5.39) for *different* gases we obtain, using Equation (5.45),

$$\Delta S = N_A k \ln\left\{\frac{V_A + V_B}{V_A}\right\} + N_B k \ln\left\{\frac{V_A + V_B}{V_B}\right\}$$

which means that Equation (5.40) remains unchanged. However, for *identical* gases we get from Equations (5.41) and (5.38), using Equation (5.45),

$$\begin{aligned}\Delta S = {} & (N_A + N_B)k\left[\frac{5}{2} + \ln\left\{\frac{V_A + V_B}{(N_A + N_B)\sigma}(2\pi mkT)^{3/2}\right\}\right] \\ & - N_A k\left[\frac{5}{2} + \ln\left\{\frac{V_A}{N_A\sigma}(2\pi mkT)^{3/2}\right\}\right] \\ & - N_B k\left[\frac{5}{2} + \ln\left\{\frac{V_B}{N_B\sigma}(2\pi mkT)^{3/2}\right\}\right]\end{aligned} \tag{5.46}$$

Since the pressure and temperature do not change during the mixture process, and since in the initial state we have thermal and mechanical equilibrium,

$$\frac{V_A}{N_A} = \frac{V_B}{N_B} = \frac{V_A + V_B}{N_A + N_B} \tag{5.47}$$

is valid, and thus

$$\Delta S = 0 \tag{5.48}$$

For two identical gases we now obtain an entropy change $\Delta S = 0$, as it should be.

Hence, the Gibbs factor $1/N!$ is indeed the correct recipe for avoiding the Gibbs paradox. From now on we will therefore always take into account the Gibbs correction factor for indistinguishable states when we count the microstates.

However, we want to emphasize that this factor is no more than a recipe to avoid contradictions of consequent classical statistical mechanics. In the case of distinguishable objects (e.g., atoms which are localized at certain grid points), the Gibbs factor must *not* be added. In classical theory the particles remain distinguishable. We will meet this inconsistency more frequently in classical statistical mechanics.

Pseudo quantum mechanical counting of Ω

Now we want to consider the ideal gas once again, to directly determine Ω by counting the quantum mechanical states of *distinguishable* particles (in Example 5.1 we have presented the classical analogon).

This will enable us to obtain an absolute number for Ω and thus an absolute entropy. In this way, it becomes possible to get a value for the unit surface (unit volume) σ_0 in phase-space, which up to now has been unknown.

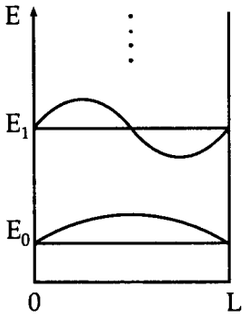


Figure 5.6. Wavefunctions and energy of a particle in a cubic box.

The quantum mechanical problem of a particle in a cubic box of length L has already been extensively discussed in volume 4 of this series (Figure 5.6). The one-particle states have the wavefunction

$$\begin{aligned}\Psi_{n_x,n_y,n_z} &= A\sin(k_x x)\sin(k_y y)\sin(k_z z)\\ &= A\sin\frac{n_x\pi x}{L}\sin\frac{n_y\pi y}{L}\sin\frac{n_z\pi z}{L}\\ n_x, n_y, n_z &= 1, 2, \ldots,\end{aligned} \tag{5.49}$$

with the corresponding single-particle energy

$$\begin{aligned}\epsilon_{n_x,n_y,n_z} &= \frac{(\hbar k)^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)\\ &= \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)\end{aligned} \tag{5.50}$$

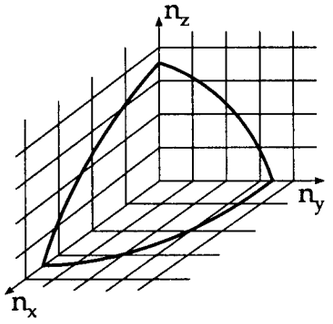


Figure 5.7. Space of quantum numbers n_i. Since the n_i in Equation (5.49) are positive numbers, they fill an octant, but only up to the surface of the sphere with the radius $R_\epsilon = \sqrt{8m\epsilon L^2/h^2}$.

In the classical case, the state of motion (microstate of a particle) is fixed by $\vec{q}$ and $\vec{p}$; in the quantum mechanical case it is fixed by the quantum numbers n_x, n_y, n_z. Each single-particle state corresponds exactly to a point in the 3-dimensional (n_x, n_y, n_z)-space. (See Figure 5.7.)

In this space, a given energy ϵ for the particle corresponds to a spherical shell with radius $\frac{L}{h}\sqrt{8m\epsilon}$. In contrast to the classical consideration in Example 5.1, however, only integer grid points which lie on this sphere are possible single-particle states for this energy ϵ. The corresponding N-particle problem is now directly solved by occupation of the single-particle states with N particles. The total energy is then determined by the $3N$ quantum numbers of the occupied states,

$$E = \frac{h^2}{8mL^2}\sum_{i=1}^{3N} n_i^2 \tag{5.51}$$

We now deal with a $3N$-dimensional space and a $(3N-1)$-dimensional energy sphere. The number of microstates Ω of a given macroscopic situation (E, V, and N, with $V = L^3$) is just the number of integer grid points on the energy surface. A glance at the figure immediately shows that Ω must be an extremely irregular function of energy. Already in the single particle case ($N = 1$) it may be possible that more, fewer, or even no grid points

TABLE 5.1 Higher states of the 3-particle system

State	Ω	Configuration
$E^* = 15 = 7*1^2 + 2*2^2$	$\binom{9}{2} = 36$	$(1)^7(2)^2$
$E^* = 17 = 8*1^2 + 1*3^2$	$\binom{9}{1} = 9$	$(1)^8(2)^0(3)^1$
$E^* = 18 = 6*1^2 + 3*2^2$	$\binom{9}{3} = 84$	$(1)^6(2)^3$
$E^* = 20 = 7*1^2 + 1*2^2 + 1*3^2$	$\binom{9}{1}\binom{8}{1} = 72$	$(1)^7(2)^1(3)^1$
$E^* = 21 = 5*1^2 + 4*2^2$	$\binom{9}{4} = 126$	$(1)^5(2)^4$

at all lie on the energy sphere, according to how many ways there are to subdivide the number $\epsilon^* = 8mL^2\epsilon/h^2$ into a sum of 3 (altogether, $3N$) quadratic numbers. In addition, we see that Ω increases very quickly with the radius of the sphere, i.e., with energy.

We want to clarify this using the example of $N = 3$ particles, i.e., 9 quantum numbers $n_1, \ldots n_9$. The lowest state results if all quantum numbers are $n_i = 1$. Here we use the notation which is already known from atomic physics and chemistry, (state) $^{\text{occupation}}$—for instance $(1)^9$; i.e., the quantum number n_1 occurs 9 times. The corresponding dimensionless energy $E^* = 8mL^2E/h^2$ is

$$E^* = 9 = 9 \times 1^2, \quad \Omega = 1, \quad \text{configuration } (1)^9 \tag{5.52}$$

The next higher state is reached if one quantum number assumes the value 2 while all the others remain at the value 1,

$$E^* = 12 = 8*1^2 + 1*2^2, \quad \Omega = 9, \quad (1)^8(2)^1 \tag{5.53}$$

Now we must take into account $\Omega = 9$ possibilities, since each of the 9 quantum numbers can assume the value 2.

Note that, strictly speaking, this is no quantum mechanical calculation. In reality, one cannot distinguish which of the particles is excited; i.e., one cannot distinguish which of the particles is actually that which has just assumed $n_i = 2$. The reason for this is that one can measure only the occupation number of a quantum state, i.e., how often a certain n_i appears. In spite of dealing with quantum mechanical states, we nevertheless use a classical statistical manner of counting. In the correct quantum statistics the indistinguishability of the particles must be taken into account *ab initio*!

The next higher states of the 3-particle system are given in Table 5.1:

As one can see in Figure 5.8, Ω is indeed a very irregular function of the parameter E^*: For a radius $\sqrt{E^*}$ of the $3N$-dimensional sphere, at one point there are 36, and at another point 9 states on the sphere. On the average, however, Ω strongly increases with energy.

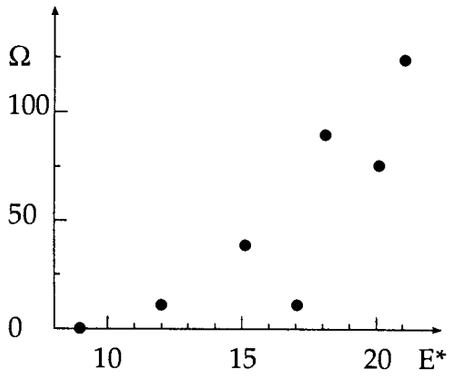


Figure 5.8. $\Omega(E^*)$: The irregularities stem from shell (quantum) effects.

If Ω strongly fluctuates with energy, the thermodynamic properties of the system (which are given by derivates of $S = \ln \Omega$) will strongly fluctuate, too, in contradiction to experience.

The irregularities of Ω simply express the fact that the system cannot assume arbitrary energy states, but can *absorb or emit energy only in discrete quanta.*

This property of the system becomes especially important if the typical energy ($\approx kT$) of a particle at temperature T is lower than or equal to the energy differences which can be estimated by $\Delta E^* = 1 = 8mL^2\Delta E/h^2$ or $\Delta E \approx h^2/8mL^2$. However, this is the case only for very small systems or very low temperatures.

Fixing the total energy of a closed system is (at least for macroscopic systems) an impossible idealization. In reality, there is always an exchange of energy with the environment, so that, strictly speaking, the only interesting number for us is the number of states Ω averaged over an energy interval ΔE. To elucidate this average, we first calculate the number of all microstates (grid points) in the interior of the energy sphere,

$$\Sigma(E, V, N) = \sum_{E' \leq E} \Omega(E', V, N) \tag{5.54}$$

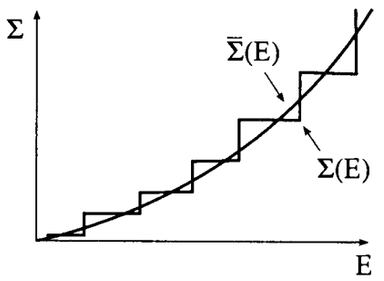


Figure 5.9. Σ and $\overline{\Sigma}$.

Now Σ is a step function, where at certain energy levels a certain number of states is added. It is easy to denote a mean function $\overline{\Sigma}$ corresponding to Σ (represented by the straight line in Figure 5.9). Differentiation of $\overline{\Sigma}$ with respect to energy yields the *mean density of states*, which gives the *mean number of states per energy interval*:

$$g(E, V, N) = \frac{\partial}{\partial E}\overline{\Sigma}(E, V, N) \tag{5.55}$$

This is in complete analogy to our classical calculation of the energy surface $\sigma(E)$ by means of $\sigma(E) = \partial\omega/\partial E$. Instead of the phase-space volume ω up to the energy E we now have the mean number of grid points $\overline{\Sigma}$ up to the energy E.

This mean number of grid points up to the energy E is, however, proportional to the volume of the positive "octant" ($n_i > 0$) up to $E = \text{const}$. Since to every grid point there corresponds a "unit cube", the mean number of grid points is just equal to the volume of the octant divided by the volume of the unit cube. Now, the volume of the unit cube in (n_x, n_y, n_z)-space just equals 1. Therefore the volume of the $3N$-dimensional sphere just equals the mean number of grid points; in principle we have the same problem as in Example 5.2, but now the constant σ_0 does not appear anywhere at all! We can immediately write down the volume of a $3N$-dimensional octant of a sphere with radius $\sqrt{E^*} = (8mEL^2/h^2)^{1/2}$. Now we have, of course, 2^{3N} "octants" (instead of 8 in the case

of $N = 1$), and with $L^2 = V^{2/3}$ instead of Equation (5.29) we now have

$$\overline{\Sigma}(E, V, N) = \left(\frac{1}{2}\right)^{3N} \left\{ \frac{\pi^{3N/2}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)} E^{*3N/2} \right\} = \left(\frac{V}{h^3}\right)^N \frac{(2\pi m E)^{3N/2}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)} \tag{5.56}$$

In Equations (5.28) and (5.29) the radius of the hypersurface $R = \sqrt{8mEv^{2/3}}$ was replaced by $R = \sqrt{8mEl^2/h^2}$. Observe that $\overline{\Sigma}$ is a dimensionless number (namely the number of all microstates of the quantum system having an energy lower than E). One directly realizes that there now corresponds exactly a volume h^{3N} of classical phase space to each microstate (cf. Equations (5.29) and (5.30)). This is in complete agreement with the uncertainty relation $\Delta q\, \Delta p \geq h$ (or $\Delta^{3N} q\, \Delta^{3N} p \geq h^{3N}$), which for each microstate requires at least a volume h^{3N} of classical phase space. So we have just recognized h^{3N} as the quantum mechanically necessary unit volume in phase space. Therefore we get

$$g(E, V, N) = \frac{\partial \overline{\Sigma}}{\partial E} = \left(\frac{V}{h^3}\right)^N \frac{(2\pi m)^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} E^{3N/2-1} \tag{5.57}$$

Observe that now *g is no longer a dimensionless number, but rather is the density of states*, i.e., the mean number of states per energy interval ΔE.

The mean number of states of energy E, $\overline{\Omega}(E)$, is then given by multiplying $g(E)$ by the width of the energy interval ΔE:

$$\overline{\Omega}(E) = g(E)\, \Delta E = \left(\frac{V}{h^3}\right)^N \frac{(2\pi m)^{3N/2}}{\Gamma(3N/2)} E^{\frac{3N}{2}-1} \Delta E \tag{5.58}$$

To eliminate the dependence on ΔE we rewrite E and ΔE using

$$E^* = \frac{8mEL^2}{h^2} \tag{5.59}$$

as E^* and ΔE^*, to be able later to take the logarithm of dimensionless numbers. We obtain

$$\begin{aligned} \overline{\Omega}(E^*) &= \left(\frac{V}{h^3}\right)^N \frac{(2\pi m)^{3N/2}}{\Gamma(3N/2)} \left(\frac{h^2}{V^{2/3} 8m}\right)^{3N/2} E^{*\frac{3N}{2}-1} \Delta E^* \\ &= \frac{\pi^{3N/2}}{\Gamma(3N/2)} \frac{1}{2^{3N}} E^{*\frac{3N}{2}-1} \Delta E^* \end{aligned} \tag{5.60}$$

To calculate thermodynamic quantities we must now form $\ln \Omega$ (or derivatives of it). However, we can subdivide $\ln \Omega$ into $\left(\frac{3N}{2} - 1\right) \ln E^* + \ln \Delta E^*$. Because $N \ln E^* \gg \ln \Delta E^*$, we can set $\ln \Delta E^* \approx 0$ and thus $\Delta E^* \approx 1$. This means that $\overline{\Omega}(E^*)$ describes the states in an energy shell at E^* of width $\Delta E^* \approx 1$. Such an energy shell must be taken into account in quantum mechanics, because the number of states is step function-like due to the shell effects (the shell distance is just $\Delta E^* = 1$—see Figure 5.9). Thus we get

$$\overline{\Omega}(E^*) \approx \frac{\pi^{3N/2}}{\Gamma(3N/2)} \frac{1}{2^{3N}} E^{*3N/2} \tag{5.61}$$

where we still have approximated $\frac{3N}{2} - 1 \approx \frac{3N}{2}$, since most frequently we will consider systems with very large particle numbers.

Rewritten for E, $\overline{\Omega}(E)$ reads

$$\overline{\Omega}(E) \approx \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{\Gamma(3N/2)} \tag{5.62}$$

Hence we really have obtained an absolute dimensionless number $\overline{\Omega}$, which in addition is independent of the width ΔE, and which is a smooth function of energy. It has also become evident that the classical restriction on the exact energy surface really is not sensible and leads to unphysical results. The reason for this is that a quantum mechanical state transferred to classical phase space requires a volume h^{3N}—it cannot be restricted to the classical energy surface! Nevertheless, for large energies ($E^* \gg 1$), i.e., if h^{3N} is very small compared to the volume of the sphere in classical phase space, the classical limit is recovered, since now each state requires only a comparatively small volume element. Nevertheless, in the classical limit the factor h^{3N} remains instead of $\sigma_0 E$!

The result (5.57), however, still has the same fault as Equations (5.33) and (5.35). The Gibbs correction factor $1/N!$ is still missing, since we have counted the particles as distinguishable. If we consider that factor and the relation $\ln \Gamma(n) = (n-1)\ln(n-1) - (n-1) \approx n \ln n - n$, we get for the absolute entropy of an ideal gas

$$S(E, V, N) = Nk\left[\frac{5}{2} + \ln\left\{\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right\}\right] \tag{5.63}$$

The constant σ of Equation (5.45) has been identified with h^3. Equation (5.63) is called the *Sackur–Tetrode equation.*

Our general prescription for the calculation of the absolute entropy of a classical system including the Gibbs correction now reads

$$S(E, V, N) = k \ln \Omega(E, V, N) \tag{5.64}$$

with (for indistinguishable objects)

$$\begin{aligned} \Omega(E, V, N) &= g(E, V, N)E \\ g(E) &= \frac{\partial \Sigma(E)}{\partial E} \\ \Sigma(E) &= \frac{1}{N!h^{3N}} \int_{H(q_\nu, p_\nu) \le E} d^{3N}p\, d^{3N}q \end{aligned} \tag{5.65}$$

Of course, this prescription implicitly contains the above-mentioned averaging procedure: One first calculates the total phase space volume up to the energy E, and then by division by h^{3N} obtains the number of quantum mechanical states within this volume. Differentiation with respect to E yields the number of states per energy interval, $g(E)$. Finally, by multiplying by E ($E^{3N/2-1} \approx E^{3N/2}$) one again obtains a dimensionless number of states.

It is clear that, strictly speaking, this procedure is exact only in the thermodynamic limit $N \to \infty$. On the other hand, it has the advantage that one can define absolute thermodynamic quantities also for classical systems, while otherwise there would always remain the unknown factor σ.

Exercise 5.3: Equations of state of the ideal gas

Use Equation (5.63) to calculate some properties of the ideal gas.

Solution First we solve Equation (5.63) for the energy:

$$E(S, V, N) = \frac{3h^2N^{5/3}}{4\pi m V^{2/3}} \exp\left\{\frac{2S}{3Nk} - \frac{5}{3}\right\}$$

The equations of state result because $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$:

$$T = \left.\frac{\partial E}{\partial S}\right|_{N,V} = \frac{2}{3Nk}E \quad \text{or} \quad E = \frac{3}{2}NkT \tag{5.66}$$

$$-p = \left.\frac{\partial E}{\partial V}\right|_{S,N} = -\frac{2}{3V}E \quad \text{or} \quad pV = NkT$$

$$\mu = \left.\frac{\partial E}{\partial N}\right|_{S,V} = E\left(\frac{5}{3N} - \frac{2S}{3N^2k}\right) = kT \ln\left\{\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right\} \tag{5.67}$$

Here we see explicitly that for the quantities s_0 and μ_0 appearing in thermodynamics the values $s_0 = \frac{5}{2}$ and $\mu_0 = 0$ result quite naturally. In thermodynamics these values had been obvious, but arbitrary (cf. Exercise 2.9).

Of course, now we also get absolute values for all other thermodynamic potentials. The free energy is for instance, using Equations (5.63) and (5.66):

$$F = E - TS = NkT\left[\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right\} - 1\right] \tag{5.68}$$

The enthalpy H and the free enthalpy G can also be easily determined. In Equations (5.67) and (5.68) the characteristic expression $(h^2/2\pi mkT)^{3/2}$ appears, which we will meet very frequently in future. The quantity

$$\lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$

is called the *thermal wavelength*. It is the wavelength of a quantum mechanical particle of energy

$$E = \pi kT = \frac{\hbar^2\underline{k}^2}{2m}$$

$$\lambda^2 = \left(\frac{2\pi}{\underline{k}}\right)^2 = \frac{h^2}{2\pi mkT}$$

where $\underline{k} = \frac{2\pi}{\lambda}$ is the wave number, which must be distinguished from the Boltzmann constant k. Obviously, the ratio of the thermal wavelength λ^3 and the volume per particle $v = V/N$ determines the number of accessible microstates. Equation (5.63) can also be directly rewritten for this quantity,

$$S(T, V, N) = Nk\left[\frac{5}{2} + \ln\left\{\frac{v}{\lambda^3}\right\}\right]$$

Further properties of the ideal gas are again obtained by differentiation of the thermodynamic potentials. For instance, we have

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V} = \frac{3}{2}Nk$$

$$C_p = \left.\frac{\partial H}{\partial T}\right|_{p,V} = \left.\frac{\partial}{\partial T}(E + pV)\right|_{p,V} = \left.\frac{\partial}{\partial T}\left(\frac{3}{2}NkT + \frac{2}{3}E\right)\right|_{p,V}$$

$$= \frac{\partial}{\partial T}\left(\frac{3}{2}NkT + NkT\right) = \frac{5}{2}Nk$$

and

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p = \frac{1}{T}, \qquad \kappa = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_T = \frac{1}{p}$$

Also, the general relation

$$C_p = C_V + TV\frac{\alpha^2}{\kappa}$$

follows immediately. Some of these relations are well known to us already from the thermodynamics part of this volume. Here, however, we have derived them solely from the statistical microscopic properties of the particles of the ideal gas. Hence we have received the equations of state of the system only from the knowledge of the Hamiltonian!

6 Ensemble Theory and Microcanonical Ensemble

Phase-space density, ergodic hypothesis

In the preceding sections we have seen how one can—at least in principle—calculate the macroscopic properties of a closed system for given E, V, and N. We now want to develop a more general formalism which we can also use to describe different situations (e.g., a system at a given temperature in a heat bath). In a given macrostate a system can assume a large number of concrete microstates. In the case of a closed system all possible microstates lie on the energy surface. Up to now, all these microstates in principle have been assumed to be equally likely: We have assumed that *all microstates of the energy surface of a closed system can be assumed with equal probability.*

This assumption is the *basic postulate of statistical mechanics.* For nonclosed systems, however, it could very well be true that microstates with a certain energy are more probable than microstates with another energy. Then the microstates may no longer be counted equally, but must be multiplied by a weighting function $\rho(q_\nu, p_\nu)$ which depends on the energy of the state. To each phase-space point (q_ν, p_ν), therefore, a weight $\rho(q_\nu, p_\nu)$ is attached, which can be interpreted as the probability density for the macrosystem to reach this phase-space point. Thus, for a closed system ρ would vanish outside the energy surface, and it would assume a constant value on the energy surface. The probability density ρ is called the *phase-space density.* It can be normalized to 1,

$$\int d^{3N}q\, d^{3N}p\rho(q_\nu, p_\nu) = 1 \tag{6.1}$$

If now $f(q_\nu, p_\nu)$ is any observable of the system, e.g., the total energy $H(q_\nu, p_\nu)$ or the angular momentum $\vec{L}(q_\nu, p_\nu)$, then in general one will observe a *mean value* $\langle f \rangle$ of this quantity in a given macrostate, in which each microstate (q_ν, p_ν) contributes corresponding to its weight $\rho(q_\nu, p_\nu)$:

$$\langle f \rangle = \int d^{3N}q\, d^{3N}p f(q_\nu, p_\nu)\rho(q_\nu, p_\nu) \tag{6.2}$$

Since each phase-space point (q_ν, p_ν) can be identified with a copy of the actual macroscopic system in a certain microstate, Equation (6.2) just is an average over a set of such identical copies (at a fixed time). The quantity $\langle f \rangle$ is thus called the *ensemble average* of the quantity f and the phase-space density ρ is the weighting function of the ensemble. *In the case of a closed system*, ρ is given by

$$\rho_{mc}(q_\nu, p_\nu) = \frac{1}{\sigma(E)} \delta(E - H(q_\nu, p_\nu)) \tag{6.3}$$

The δ-function ensures that all points which are not on the energy surface with the area $\sigma(E)$ have the weight 0, while the factor $1/\sigma$ is for normalization.

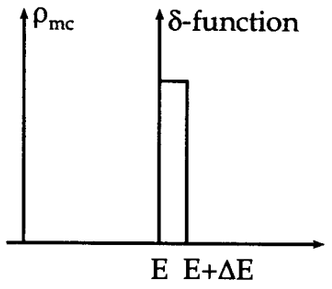


Figure 6.1. Microcanonical phase–space density.

The phase-space density of a closed system corresponds to a certain ensemble of possible microstates and is called a *microcanonical ensemble*, which we denote by the index *mc*. Other systems will, of course, have different phase-space densities, which we still have to calculate. (See Figure 6.1.)

For practical calculations, however, Equation (6.3) is very inconvenient because of the δ-function, which has a complicated argument. As in the preceding sections, it is therefore better to allow for a small energy uncertainty ΔE. One sets

$$\rho_{mc} = \begin{cases} \text{const.} & E \leq H(q_\nu, p_\nu) \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{6.4}$$

The constant in this case is determined by normalization,

$$\int d^{3N}q\, d^{3N}p \rho_{mc} = \text{const.} \int_{E \leq H(q_\nu, p_\nu) \leq E + \Delta E} d^{3N}q\, d^{3N}p$$
$$= 1 \tag{6.5}$$

This integral, however, is well known to us (cf. Equation (5.65)), and we have (without the Gibbs factor $1/N!$)

$$\text{const.} = (\Omega(E, V, N)h^{3N})^{-1} \tag{6.6}$$

Since the factor h^{3N} will appear very frequently, from now on we will include it in the volume element of phase space. (Recall that the Gibbs correction factor appears only if one afterwards corrects for the indistinguishability of the particles.) From now on instead of Equation (6.1) we will write

$$\frac{1}{h^{3N}} \int d^{3N}q\, d^{3N}p \rho(q_\nu, p_\nu) = 1 \tag{6.7}$$

and, respectively, for Equation (6.2),

$$\langle f \rangle = \frac{1}{h^{3N}} \int d^{3N}q\, d^{3N}p f(q_\nu, p_\nu)\rho(q_\nu, p_\nu) \tag{6.8}$$

This has the advantage that the *phase-space density now is a dimensionless number*. The phase-space density of the microcanonical ensemble reads, normalized (again without

Gibbs' factor):

$$\rho_{mc} = \begin{cases} \dfrac{1}{\Omega} & E \leq H(q_\nu, p_\nu) \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{6.9}$$

Basic to ensemble theory is the further assumption that all thermodynamic quantities of state can be written as an ensemble average of a suitable microscopic observable $f(q_\nu, p_\nu)$. In the following we must therefore not only determine the phase-space density for a nonclosed system, but also the function $f(q_\nu, p_\nu)$, which corresponds to a certain quantity of state.

First, however, we want to pursue some general considerations concerning the ensemble average. Up to now, we have started from some basic assumptions which cannot be directly derived from classical mechanics. On the other hand, the solution of Hamilton's equations of motion of a system $(q_\nu(t), p_\nu(t))$ as a function of time should uniquely fix all imaginable observables of the system.

However, the time dependence of the actual phase-space trajectory is of no importance for the ensemble average. Instead, we have just related a probability to each phase-space point (q_ν, p_ν) that this special microstate can be reached. Now in equilibrium, all thermodynamic (macroscopical) observables are independent of time. In principle, these quantities therefore should be calculable as a time average of the real phase-space trajectory, for instance, according to

$$\overline{f} = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt f(q_\nu(t), p_\nu(t)) \tag{6.10}$$

where the time dependence $(q_\nu(t), p_\nu(t))$ is fixed by Hamilton's equations of motion. The time average along the phase-space trajectory is of no essential practical value, since for its calculation the complete solution of the equations of motion is needed. However, it is of principle significance. Namely, if one could mathematically prove that the time average essentially leads to the same result as the ensemble average, then our preceding assumptions could be founded purely microscopically.

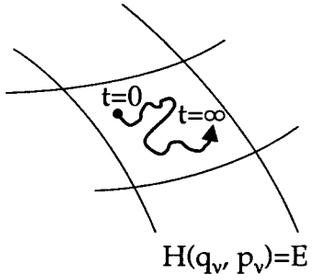


Figure 6.2. Phase–space trajectory.

The time average $\overline{f}$ and the ensemble average $\langle f \rangle$ for a closed system at a given energy would certainly be identical if during its time evolution the phase-space trajectory passed through each point of the energy surface an equal number of times (e.g., once—sufficient condition). (See Figure 6.2.) This condition, which was introduced by Boltzmann in 1871, is called the *ergodic hypothesis*.* In this case, an average over all times, of course, would exactly correspond to an average over all points of the surface with equal weights. That such ergodic systems exist, in principle, is shown by our example of the one-dimensional harmonic oscillator. As we know, during one period each point of the energy ellipse is passed just once.

For higher dimensional systems, however, one can prove mathematically that the phase-space trajectory, in principle, can never pass through all points of the energy surface. The reason for this is that on the one hand Hamilton's equations of motion always have a unique

*For a detailed, but very mathematical discussion of this problem we refer to I.E. Farquhan: *Ergodic Theory in Statistical Mechanics*, Interscience Publishers, New York 1964.

solution, so that the phase-space trajectory can never cross itself, but that on the other hand it is problematic to map a one-dimensional time interval onto an N-dimensional surface element. Now for the identity of time averages and ensemble averages, it is not necessary that the phase-space trajectory really pass through every point of the energy surface. It would also be sufficient if it came arbitrarily close to each point. *This assumption is the so-called quasi ergodic hypothesis.*

Unfortunately, up to now all attempts to base ensemble theory strictly on classical mechanics have failed. Therefore, we must pose our assumptions axiomatically at the starting point of statistical mechanics.

Liouville's theorem

We want to examine some general properties of the phase-space density $\rho(q_\nu, p_\nu)$. Since the ensemble average for a system in thermodynamic equilibrium must be time independent, the phase-space density must not explicitly depend on time. In this case ($\partial\rho/\partial t = 0$), one deals with stationary ensembles. However, later on we will see that the concept of phase-space densities can also be used to describe the dynamics of processes. To ensure complete generality we therefore also want to allow for an explicit time dependence in $\rho(q_\nu, p_\nu, t)$, where, however, for thermodynamics we need only time-independent ensembles.

If at a concrete time t_0 a system is in the concrete microstate q_ν, p_ν, then during the course of time this system will evolve to other microstates $q_\nu(t)$, $p_\nu(t)$. Along the phase-space trajectory, the phase-space density changes with time. The temporal change can, in general, be written according to Equation (5.4):

$$\frac{d}{dt}\rho(q_\nu(t), p_\nu(t), t) = \frac{\partial}{\partial t}\rho(q_\nu(t), p_\nu(t), t) + \{\rho, H\} \tag{6.11}$$

If we now consider a phase-space volume ω, each phase–space point of this volume element can be assumed to be the starting point of a phase-space trajectory. Note that the trajectories are allowed to cross if they are not identical.

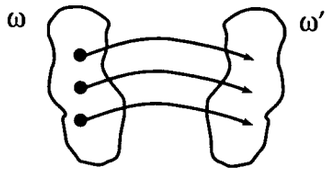


Figure 6.3. Flux in phase space.

In the course of time, all systems (as schematically pointed out in Figure 6.3) will move to different phase-space points, mapping the volume element ω at time t to another volume element ω' at time t'. In this process no points are lost and also no points are gained. The mapping can therefore be interpreted as the flux of an incompressible fluid without sources or sinks.

The rate at which the systems "flow out" of the finite volume ω is given by the flux through the surface:

$$\frac{\partial}{\partial t}\int_\omega d\omega\rho = -\int_\sigma \rho(\vec{v}\cdot\vec{n})\,d\sigma \tag{6.12}$$

where $\vec{v}$ is the flux velocity, which is of course given by the vector $(\dot{q}_\nu, \dot{p}_\nu)$. The sign corresponds exactly to an outwardly directed normal unit vector. According to Gauss'

theorem, Equation (6.12) can be rewritten as

$$\int_{\omega} d\omega \left(\frac{\partial}{\partial t} \rho + \operatorname{div}(\rho \vec{v}) \right) = 0 \tag{6.13}$$

The divergence here reads explicitly

$$\operatorname{div}(\rho \vec{v}) = \sum_{\nu=1}^{3N} \left\{ \frac{\partial}{\partial q_\nu} (\rho \dot{q}_\nu) + \frac{\partial}{\partial p_\nu} (\rho \dot{p}_\nu) \right\} \tag{6.14}$$

since phase space has $3N$ coordinates and $3N$ momenta altogether. Thus, along a phase-space trajectory the continuity equation

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \vec{v}) = 0 \tag{6.15}$$

holds, since the considered volume ω is arbitrary. On the other hand, from Equation (6.14) we obtain, using Hamilton's equations of motion,

$$\begin{aligned} \operatorname{div}(\rho \vec{v}) &= \sum_{\nu=1}^{3N} \left\{ \frac{\partial \rho}{\partial q_\nu} \dot{q}_\nu + \frac{\partial \rho}{\partial p_\nu} \dot{p}_\nu + \rho \left(\frac{\partial \dot{q}_\nu}{\partial q_\nu} + \frac{\partial \dot{p}_\nu}{\partial p_\nu} \right) \right\} \\ &= \sum_{\nu=1}^{3N} \left\{ \frac{\partial \rho}{\partial q_\nu} \frac{\partial H}{\partial p_\nu} - \frac{\partial \rho}{\partial p_\nu} \frac{\partial H}{\partial q_\nu} \right\} + \rho \sum_{\nu=1}^{3N} \left\{ \frac{\partial^2 H}{\partial q_\nu \partial p_\nu} - \frac{\partial^2 H}{\partial p_\nu \partial q_\nu} \right\} \end{aligned} \tag{6.16}$$

or

$$\operatorname{div}(\rho \vec{v}) = \{\rho, H\} \tag{6.17}$$

because the last term in Equation (6.16) vanishes. Therefore, we now have for Equations (6.15) and (6.11):

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \tag{6.18}$$

The total time derivative of the phase-space density thus vanishes along a phase-space trajectory. This is *Liouville's theorem* (1838). For stationary ensembles which do not explicitly depend on time ($\partial \rho / \partial t = 0$), it follows that

$$\{\rho, H\} = \sum_{\nu=1}^{3N} \left(\frac{\partial \rho}{\partial q_\nu} \frac{\partial H}{\partial p_\nu} - \frac{\partial \rho}{\partial p_\nu} \frac{\partial H}{\partial q_\nu} \right) = 0 \tag{6.19}$$

As we know from classical mechanics, this means that ρ is a constant of the motion and depends only on conserved quantities. For instance, $\rho(H(q_\nu, p_\nu))$ fulfills Equation (6.19):

$$\frac{\partial \rho}{\partial q_\nu} \frac{\partial H}{\partial p_\nu} - \frac{\partial \rho}{\partial p_\nu} \frac{\partial H}{\partial q_\nu} = \frac{\partial \rho}{\partial H} \left(\frac{\partial H}{\partial q_\nu} \frac{\partial H}{\partial p_\nu} - \frac{\partial H}{\partial p_\nu} \frac{\partial H}{\partial q_\nu} \right) = 0 \tag{6.20}$$

The microcanonical ensemble

Up to now, we have more or less guessed the phase-space density of a closed system for a given total energy and justified this guess by success. *Now we want to prove that a constant phase-space density on the energy surface is the most probable one for a system.* The method which we use here also will be very useful for us later, in the derivation of probability densities for other systems (especially for quantum systems).

Therefore, we consider $\mathcal{N}$ identical copies of our closed system (an ensemble), each with the macroscopic natural quantities of state (E, V, N). Do not confuse the number $\mathcal{N}$ of systems with the number N of particles in each system. Each of the $\mathcal{N}$ systems at a fixed time is in a certain microstate (q_ν, p_ν). In general, these microstates are different from each other, but they must all lie on the energy surface.

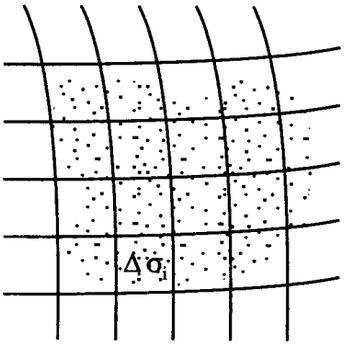


Figure 6.4. Subdivision of the energy hypersurface of phase space.

Now we subdivide the energy surface into equally large surface elements $\Delta\sigma_i$, which we enumerate (Figure 6.4). Each of these surface elements contains a number n_i of systems (bundles of microstates). If we choose the surface elements to be sufficiently small, then each of these elements corresponds exactly to one microstate. However, now we consider such $\Delta\sigma_i$, which cover n_i microstates (systems). Altogether, we must of course have

$$\mathcal{N} = \sum_i n_i \tag{6.21}$$

The number of systems n_i in a certain surface element $\Delta\sigma_i$ corresponds exactly to the weight of the corresponding microstate in the ensemble. The number $n_i/\mathcal{N}$ can be interpreted as the probability for microstate i to lie in $\Delta\sigma_i$. The probability $p_i = n_i/\mathcal{N}$ therefore corresponds to the expression $\rho(q_\nu, p_\nu)\, d^{3N}q\, d^{3N}p$ in the continuous formulation.

A certain distribution $\{n_1, n_2, \ldots\}$ of the $\mathcal{N}$ systems over the surface elements can be achieved in different ways.

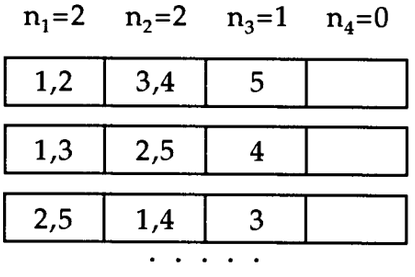


Figure 6.5. Distribution of systems on surface elements.

If we enumerate the $\mathcal{N}$ systems, for instance for $\mathcal{N} = 5$ and 4 surface elements, with $n_1 = 2$, $n_2 = 2$, $n_3 = 1$, and $n_4 = 0$, then there are different possibilities, as indicated in Figure 6.5. The calculation of the total number of possibilities for a certain distribution $\{n_i\}$ is a simple combinatorial problem: There are exactly $\mathcal{N}!$ ways to enumerate the systems differently, but in each case $n_i!$ exchanges in one phase-space cell do not give a new case. If, for instance, in our example in cell 1 the numbers 1 and 2 are exchanged, obviously nothing has changed at all.

The *total number of ways* $W\{n_i\}$ to generate a certain distribution $\{n_i\}$ is therefore given by

$$W\{n_i\} = \frac{\mathcal{N}!}{\prod_i n_i!} \tag{6.22}$$

if i runs over all surface elements.

Now we ask for the probability $W_{\text{tot}}\{n_i\}$ of finding a distribution $\{n_i\}$ on the surface element σ_i. Let ω_i be the probability of finding *one* system within the surface element $\Delta\sigma_i$. Then the probability of having exactly n_i systems in $\Delta\sigma_i$ is $(\omega_i)^{n_i}$, because the systems in the ensemble are statistically independent from each other. For the same reason, we get for the probability distribution $W_{\text{tot}}\{n_i\}$ of the distribution $\{n_i\}$:

$$W_{\text{tot}}\{n_i\} = \mathcal{N}! \prod_i \frac{(\omega_i)^{n_i}}{n_i!} \tag{6.23}$$

Now we ask for the most probable distribution $\{n_i\}^*$ of the $\mathcal{N}$ systems over the phase-space cells (surface elements). Hence we must determine the maximum of Equation (6.23). Because of the inconvenient product form, it is more advantageous to first calculate the maximum of $\ln W_{\text{tot}}\{n_i\}$ which, of course, is identical to that of $W_{\text{tot}}\{n_i\}$. For $\mathcal{N} \to \infty$, however, all $n_i \to \infty$ (in the case of finite surface elements), and therefore all factors may be approximated by $\ln n! \approx n \ln n - n$,

$$\begin{aligned} \ln W_{\text{tot}} &= \ln \mathcal{N}! + \sum_i (n_i \ln \omega_i - \ln n_i!) \\ &= \mathcal{N} \ln \mathcal{N} - \mathcal{N} + \sum_i \{n_i \ln \omega_i - (n_i \ln n_i - n_i)\} \end{aligned} \tag{6.24}$$

If $\ln W_{\text{tot}}$ is maximal, then the total differential must vanish. Since the number $\mathcal{N}$ is constant, it must hold that

$$d \ln W_{\text{tot}} = -\sum_i (\ln n_i - \ln \omega_i)\, dn_i = 0 \tag{6.25}$$

If all the dn_i were independent from each other, each coefficient in Equation (6.25) would have to vanish. However, the dn_i are related to each other by Equation (6.21). Now we know how to solve such extreme value problems using constraints. We form the differential of Equation (6.21) and multiply it by an unknown Lagrange multiplier λ:

$$\lambda\, d\mathcal{N} = \lambda \sum_i dn_i = 0 \tag{6.26}$$

This equation is added to Equation (6.25), resulting in

$$\sum_i (\ln n_i - \ln \omega_i - \lambda) dn_i = 0 \tag{6.27}$$

as a condition for an extreme value of $\ln W_{\text{tot}}$. Now we can consider all dn_i to be independent from each other, if subsequently Equation (6.21) is fulfilled by a convenient choice of the Lagrange multiplier λ. Therefore, each coefficient in Equation (6.27) must vanish separately:

$$\ln n_i = \lambda + \ln \omega_i \qquad \text{or} \qquad n_i = \omega_i e^{\lambda} = \text{const.} \tag{6.28}$$

Now λ can, in principle, be determined from Equation (6.21). However, this is not so interesting for us. The significance of Equation (6.28) results from the fact that the number of systems in the surface element $\Delta\sigma_i$ is just proportional to the probability ω_i, thus to the probability of finding a system within $\Delta\sigma_i$. This is plausible.

Now one of the basic assumptions of statistical physics is that all microstates (all phase-space points) are, in principle, equally likely, and thus have the same probability ω_i. Therefore the ω_is are simply proportional to the corresponding surface element $\Delta\sigma_i$. This means that the probability ω_i of finding a system in the surface element i is proportional to its size $\Delta\sigma_i$. If all surface elements are chosen to be of equal size and very small, the number n_i of systems must be equal in all surface elements.

So we have recognized a constant phase-space density on the energy surface as the most probable possibility. Of course, our considerations remain right, if instead of the energy surface we consider a very thin energy shell between E and $E + \Delta E$, and we have

$$p_i = \frac{n_i}{\mathcal{N}} = \begin{cases} \text{const.} & H = E \\ 0 & \text{otherwise} \end{cases}$$

$$\Rightarrow \rho_{mc} = \begin{cases} \text{const.} & E \leq H(q_\nu, p_\nu) \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{6.29}$$

Here p_i is understood to be the probability of finding a system in the ensemble in the microstate (surface element) with number i.

Analogously, $\rho_{mc}(q_\nu, p_\nu)\, d^{3N}q_\nu\, d^{3N}p_\nu$ is the probability of finding a system (a microstate) within the phase-space volume element $d^{3N}q_\nu\, d^{3N}p_\nu$.

Entropy as an ensemble average

We have not yet specified which functions $f(q_\nu, p_\nu)$ have to be chosen to calculate a certain thermodynamic quantity as an ensemble average,

$$\langle f \rangle = \frac{1}{h^{3N}} \int d^{3N}q\, d^{3N}p f(q_\nu, p_\nu)\, \rho(q_\nu, p_\nu) \tag{6.30}$$

It is not difficult to denote a function $f(q_\nu, p_\nu)$ for the microcanonical ensemble, the ensemble average of which just yields the entropy. First, the microcanonical phase-space density is given by

$$\rho_{mc} = \begin{cases} \dfrac{1}{\Omega} & E \leq H(q_\nu, p_\nu) \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{6.31}$$

On the other hand, we have

$$S(E, V, N) = k \ln \Omega(E, V, N) \tag{6.32}$$

Formally, the entropy is therefore

$$S(E, V, N) = \frac{1}{h^{3N}} \int d^{3N}q\, d^{3N}p \rho_{mc}(q_\nu, p_\nu)\, (-k \ln \rho_{mc}(q_\nu, p_\nu)) \tag{6.33}$$

To prove this, insert Equation (6.31) into Equation (6.33), and bear in mind that $\rho \ln \rho = 0$ for $\rho = 0$,

$$S(E, V, N) = \frac{1}{h^{3N}} \int_{E \le H(q_\nu, p_\nu) \le E + \Delta E} d^{3N}q \, d^{3N}p \, \frac{1}{\Omega} \left(-k \ln \frac{1}{\Omega} \right) \tag{6.34}$$

The integrand is a constant on the energy shell and can therefore be pulled out of the integral:

$$S(E, V, N) = \frac{1}{\Omega} k \ln \Omega \frac{1}{h^{3N}} \int_{E \le H(q_\nu, p_\nu) \le E + \Delta E} d^{3N}q \, d^{3N}p \tag{6.35}$$

Inserting here Equation (5.65) (without the Gibbs factor $1/N!$, which has already been omitted in Equation (6.30)), we get

$$S(E, V, N) = \frac{1}{\Omega} k \ln \Omega \cdot \Omega = k \ln \Omega \tag{6.36}$$

as it should be. Equation (6.33) is thus only a slightly more complicated formulation of Equation (6.32). However, it has the great advantage that it can be easily transformed to other phase-space densities. In general, we write

$$S = \langle -k \ln \rho \rangle \tag{6.37}$$

Thus, *entropy is the ensemble average of the logarithm of the phase-space density.* Because of the fundamental significance of this statement we want to discuss Equation (6.37) in more detail.

The uncertainty function

Consider an experiment that involves random events, e.g., throwing dice with different possible outcomes. Let there be a probability p_i attached to each of the i possible outcomes of the experiment. In the case of an ideal die one has $p_i = 1/6$ for $i = 1, \ldots, 6$. In a series of $\mathcal{N}$ casts ($\mathcal{N} \to \infty$), all numbers from 1 to 6 will appear an equal number of times, namely, on the average exactly $n_i = p_i \mathcal{N}$ times.

If instead of the ideal die we take a manipulated one, which for instance may have the probabilities $p_1 = p_2 = p_3 = p_4 = p_5 = 1/10$ and $p_6 = 5/10$, then a series of casts will yield the number 6 five times as often as any one of the other numbers. The result of a cast with the modified die can thus be predicted with a larger certainty than that of an ideal die. In the extreme case of a special die with $p_1 = p_2 = p_3 = p_4 = p_5 = 0$ and $p_6 = 1$ one can even predict with *absolute certainty* what the next throw will yield.

In other words, the equal probability of all possibilities, $p_i = \text{const.}$ (equal distribution), provides the situation with the largest uncertainty on the outcome of an experiment, while all other distributions result in a larger certainty (lower uncertainty) of the prediction. Thus there arises in mathematical statistics the question whether there is a unique measure for the predictability (uncertainty) of a random event which also can be used to compare different kinds of random events.

First, we want to reflect on what properties such a measure should have. The experiment is defined in the mathematical sense by denoting the probabilities p_i of the events. The uncertainty function H should only be a function of these probabilities:

$$H = H(p_i), \qquad i = 1, \ldots \text{ (possible outcome of the experiment)} \tag{6.38}$$

Furthermore, the uncertainty of a sure experiment, that is, one whose outcome is certain, should be $H = 0$; for instance, the outcome of the throw of the superdie $p_1 = \cdots = p_5 = 0$, $p_6 = 1$ has no uncertainty in it whatsoever. We thus require that

$$H(p_1, p_2, \ldots) = 0 \qquad \text{for} \quad p_1 = 0, \ldots, \; p_{i-1} = 0, \; p_i = 1, \; p_{i+1} = 0, \; \ldots \tag{6.39}$$

since an experiment with such a probability distribution always yields the result i.

In addition, the measure for the uncertainty must be independent of the enumeration of the p_i. Therefore, we require for the exchange of two probabilities that

$$H(\ldots, p_i, \ldots, p_k, \ldots) = H(\ldots, p_k, \ldots, p_i, \ldots) \tag{6.40}$$

In the case of the dice we have already seen that the equal distribution $p_i = \text{const.}$ is obviously the one with the largest uncertainty. Therefore we require that

$$H = H_{\max} \qquad \text{for} \quad \textit{all } p_i = \text{const.} \tag{6.41}$$

Finally, we must say something about how to calculate the uncertainty H(I *AND* II) of an experiment that consists of the logical conjunction of two experiments I and II, with uncertainties H(I) and H(II). Each outcome of the conjoined experiment is of the form (event i for experiment I) *and* (event j for experiment II). If experiments I and II are independent, we require that

$$H(\text{I AND II}) = H(\text{I}) + H(\text{II}) \tag{6.42}$$

This definition is recommended by the fact that H vanishes for a sure experiment. If, for example, experiment I is a sure experiment, H(I) $= 0$, and experiment II is an experiment having any uncertainty, then by the *AND*-combination of both experiments the total uncertainty is not increased. Therefore the multiplication of the uncertainties in the case of *AND*-combinations (in contrast to the probabilities) is not sensible. Now one can prove mathematically that the conditions (6.38–42) uniquely fix the uncertainty function. It reads

$$H(p_i) = -\sum_i p_i \ln p_i \tag{6.43}$$

We do not want to prove the uniqueness of Equation (6.43) up to a (positive) multiplicative constant, but we want to show that it fulfills conditions (6.38–42).

Condition (6.38) is trivial, while Condition (6.39) is at once clear because $\ln p_i = 0$ for $p_i = 1$, and because $p_j \ln p_j = 0$ for $p_j = 0$. Condition (6.40) is trivial as well, since in Condition (6.43) the enumeration of the summation index may be changed. Condition (6.41) is now easily shown by forming the complete differential,

$$dH = -\sum_i (\ln p_i + 1) \, dp_i \tag{6.44}$$

This must vanish for $H = H_{\max}$, but because of

$$\sum_i p_i = 1 \tag{6.45}$$

the p_i are not all independent from each other. In complete analogy to the preceding section, this extreme-value problem leads to the statement $p_i = \text{const.}$ with the aid of the Lagrange multipliers. Finally there results condition (6.42) with the probabilities p_i for experiment I and q_k for experiment II, since the probabilities of statistically independent events multiply in the case of *AND*-combinations:

$$\begin{aligned} H(\text{I AND II}) &= -\sum_i \sum_k (p_i q_k) \ln(p_i q_k) \\ &= -\sum_i \sum_k (p_i q_k) \ln p_i - \sum_i \sum_k (p_i q_k) \ln q_k \\ &= -\sum_i p_i \ln p_i - \sum_k q_k \ln q_k \\ &= H(\text{I}) + H(\text{II}) \end{aligned} \tag{6.46}$$

where $\sum_i p_i = 1$ and $\sum_k q_k = 1$ has been used.

Condition (6.42) corresponds to the extensiveness of entropy. If the system moves from a state with a low number of microstates into a more probable state with more microstates, then the uncertainty and thus also the entropy become larger, too.

Example 6.1: Motion in one dimension

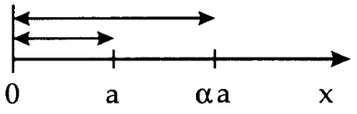


Figure 6.6.

We consider a particle which can move only in the x-direction. Let the particle be restricted to the interval $0 \leq x \leq a$ and let it move statistically forward and backward. The probability density $\rho(x)$ of finding the particle at the point x is given by

$$\rho(x) = \begin{cases} 1/a & 0 \leq x \leq a \\ 0 & \text{otherwise} \end{cases}$$

The corresponding uncertainty is

$$H = -\int_0^a dx \rho \ln \rho = \ln a$$

If the interval is enlarged by a factor $\alpha > 1$, we obtain

$$\rho'(x) = \begin{cases} 1/\alpha a & 0 \leq x \leq \alpha a \\ 0 & \text{otherwise} \end{cases}$$

and hence

$$H' = -\int_0^{\alpha a} dx \rho' \ln \rho' = \ln a + \ln \alpha$$

Thus, the uncertainty increases in an exactly defined manner, if $\alpha > 1$ (or decreases, in the case $\alpha < 1$).

Remark: For simplicity we have omitted momentum space. Nevertheless, in doing so we do not make any mistake, since we can identify the more general p_i with $\rho(x)$.

Example 6.2: The ultrarelativistic gas

Now we want to calculate the thermodynamic properties of an ultrarelativistic classical gas with the aid of the microcanonical ensemble. Such a gas consists of massless particles that move with the velocity of light (e.g., photons). According to the relativistic energy–momentum relation one has

$$\epsilon = (\vec{p}^2c^2 + m^2c^4)^{1/2} \rightarrow \epsilon = |\vec{p}|c \qquad \text{for} \quad m = 0$$

The ultrarelativistic gas is also frequently used as an easily calculable model for particles with mass $m \neq 0$, if the available energy per particle $\epsilon \gg mc^2$, or equivalently, if the temperature is very high, so that the rest energy mc^2 can be neglected compared to the kinetic energy.

For practical applications we start again with

$$S(E, V, N) = k \ln \Omega(E, V, N)$$

with

$$\Omega(E, V, N) = \frac{1}{h^{3N}N!} \int_{E \leq H(q_\nu, p_\nu) \leq E + \Delta E} d^{3N}q \, d^{3N}p$$

where, because of the indistinguishability of the particles, the Gibbs correction factor $1/N!$ must be taken into account.

The Hamiltonian H of the system reads

$$H(q_\nu, p_\nu) = \sum_{\nu=1}^{N} c \left(p_{x,\nu}^2 + p_{y,\nu}^2 + p_{z,\nu}^2\right)^{1/2}$$

As in the case of the ideal gas we first calculate the quantity Σ instead of Ω,

$$\Sigma(E, V, N) = \frac{1}{h^{3N}N!} \int_{H(q_\nu, p_\nu) \leq E} d^{3N}q \, d^{3N}p$$

Since the Hamiltonian does not depend on the coordinates, the integral over $d^{3N}q$ just yields the container volume V^N, and thus

$$\Sigma(E, V, N) = \frac{V^N}{h^{3N}N!} \int_{H(p_\nu) \leq E} d^{3N}p \tag{6.47}$$

We must still determine the volume of the geometrical shape

$$\sum_{i=1}^{N} |\vec{p}_i|c \leq E \tag{6.48}$$

in $3N$-dimensional momentum space. Because of the square root in $|\vec{p}_i|$, the left side of Equation (6.48) decomposes into a sum of N square roots, which makes the geometry of the shape nearly inconceivable. We shall therefore use a rather plausible approximation. (Later on we shall calculate the ultrarelativistic gas in another way exactly.) On averaging over many

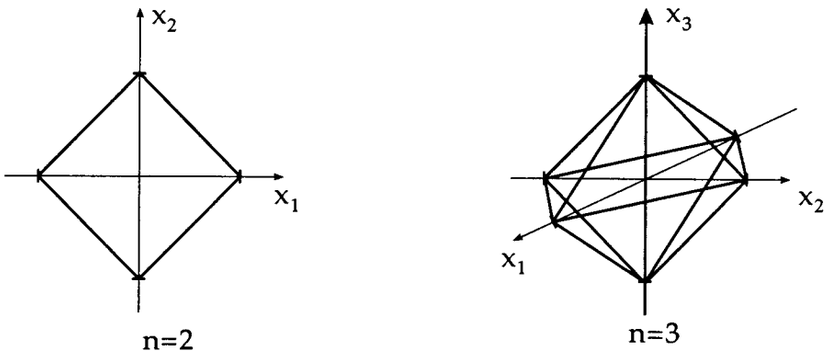


Figure 6.7. Volumes that fulfill Equation (6.51).

phase-space points, we have

$$\langle \vec{p}^2 \rangle = 3\langle p_x^2 \rangle = 3\langle p_y^2 \rangle = 3\langle p_z^2 \rangle$$

since no direction in space is preferred, i.e.,

$$\sqrt{\langle \vec{p}^2 \rangle} = \frac{\sqrt{3}}{3}\left(\sqrt{\langle p_x^2 \rangle} + \sqrt{\langle p_y^2 \rangle} + \sqrt{\langle p_z^2 \rangle}\right)$$

Therefore we make the approximation

$$\epsilon = c\left(p_x^2 + p_y^2 + p_z^2\right)^{1/2} \approx \frac{c}{\sqrt{3}}\left(|p_x| + |p_y| + |p_z|\right)$$

Then condition (6.48) reads

$$\sum_{i=1}^{3N} |p_i| \frac{c}{\sqrt{3}} \leq E \tag{6.49}$$

if the momentum components are enumerated from 1 to $3N$. Equation (6.49) now represents a regular geometric body in $3N$ dimensions. (In the case of the classical ideal gas we dealt with a sphere.) Now Equation (6.47), with the substitution $x_i = p_i c/\sqrt{3}E$, gives

$$\Sigma(E, V, N) = \frac{V^N}{h^{3N} N!}\left(\frac{\sqrt{3}E}{c}\right)^{3N} \int_{\sum_{i=1}^{3N} |x_i| \leq 1} d^{3N}x \tag{6.50}$$

The last integral only depends on the dimensionality of the space, which we want to abbreviate by $3N = n$. For $n = 2$ or 3 dimensions the condition reads, respectively,

$$|x_1| + |x_2| \leq 1 \qquad \text{or} \qquad |x_1| + |x_2| + |x_3| \leq 1 \tag{6.51}$$

The corresponding bodies (cf. Figure 6.7) are point-symmetric (axially symmetric) with respect to the origin (the coordinate axis). It is therefore sufficient to calculate the volume of the body in the positive octant ($0 \leq x_i \leq 1$) and then multiply the volume by the number 2^n of octants. When we limit the volume to the region of positive x_i (Figure 6.8), we deal with an n-dimensional simplex, the set of points of which is given by:

$$\vec{r} = \sum_{i=1}^{n} x_i \vec{e}_i \qquad \text{with} \qquad \sum_{i=1}^{n} x_i \leq 1 \text{ and } x_i \in [0, 1] \tag{6.52}$$

(for the dimensions $n = 0, 1, 2, 3$ the corresponding simplices are just points, edges, triangular surfaces, and tetrahedra, respectively).

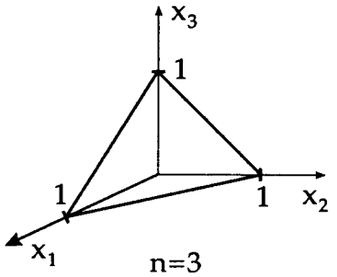


Figure 6.8. Positive octant for $n = 3$

As one can see, the basal hypersurface of the body ($x_n = 0$) is just given by the corresponding $(n-1)$-dimensional simplex. This suggests a recursion formula for the volume. One can interprete the body as a generalized cone for which in $n-1$ dimensions the formula

$$\text{volume} = \frac{1}{n}\,\text{area} \times \text{height} \tag{6.53}$$

is valid. (The proof for this equation follows later.)

However, the basal surface is just the volume of the $(n-1)$-dimensional simplex, while its height is $h = 1$. (The height of the simplex must be calculated at $x_{n-1} = \cdots = x_1 = 0$, which with the aid of Equation (6.52) leads to $x_n = h = 1$.) Therefore we have

$$I_n = \frac{1}{n} I_{n-1}$$

$$I_n = \int_{\sum_{i=1}^{n} x_i \le 1} d^n x, \qquad x_i \in [0, 1]$$

This recursion formula immediately leads to

$$I_n = \frac{1}{n!}$$

The total volume of the body with 2^n octants (i.e., now $x_i \in [-1, 1]$) is given by

$$\int_{\sum_{i=1}^{n} |x_i| \le 1} d^n x = \frac{2^n}{n!}$$

Inserting this into Equation (6.50) yields, with $n = 3N$,

$$\Sigma(E, V, N) = \frac{V^N}{h^{3N} N!} \left(\frac{\sqrt{3}E}{c}\right)^{3N} \frac{2^{3N}}{(3N)!}$$

Then g is given by differentiation with respect to energy (cf. Equation (5.65)):

$$g(E, V, N) = \frac{\partial \Sigma(E, V, N)}{\partial E} = \frac{V^N}{h^{3N} N!} \left(2\frac{\sqrt{3}}{c}\right)^{3N} \frac{E^{3N-1}}{(3N-1)!}$$

Here we can assume $N \gg 1$, and thus $3N - 1 \approx 3N$. The number of states in a small energy interval between E and $E + \Delta E$ is $\Omega = g \cdot \Delta E$. However, since nearly all states lie within this interval, one can as well set $\Omega = g \cdot E$, and one obtains

$$S(E, V, N) = k \ln \Omega(E, V, N) = k \ln \left\{ \frac{V^N}{N!} \left(\frac{2\sqrt{3}}{hc}^{3N}\right) \frac{E^{3N}}{(3N!)} \right\}$$

$$= Nk \ln \left\{ V \left(\frac{2\sqrt{3}E}{hc}^{3}\right) \right\} - k \ln N! - k \ln(3N)!$$

Using Stirling's formula $\ln N! \approx N \ln N - N$ this can be rewritten,

$$S = Nk \ln \left\{ V \left(\frac{2\sqrt{3}E}{hc} \right)^3 \right\} - Nk \ln N - 3Nk \ln 3N + 4Nk$$

$$= Nk \left[\ln \left\{ V \left(\frac{2\sqrt{3}E}{hc} \right)^3 \right\} - \ln N - \ln 3N^3 + 4 \right]$$

Thus

$$S(E, V, N) = k \ln \Omega(E, V, N) = Nk \left[4 + \ln \left\{ \frac{V}{N} \left(\frac{2E}{\sqrt{3}Nhc} \right)^3 \right\} \right] \tag{6.54}$$

This yields the following equations of state for the ultrarelativistic ideal gas:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{V,N} = 3Nk \frac{1}{E}$$

$$E = 3NkT \tag{6.55}$$

The energy at a given temperature is therefore twice as large as in the case of the ideal gas.

$$\frac{p}{T} = \left. \frac{\partial S}{\partial V} \right|_{E,N} = \frac{Nk}{V}$$

$$pV = NkT \tag{6.56}$$

Combining Equations (6.55) and (6.56) yields

$$p = \frac{1}{3} \frac{E}{V}$$

Thus, the pressure is one-third of the energy density, while for an ideal gas we have $p = \frac{2}{3} E/V$. The chemical potential μ is given by

$$-\frac{\mu}{T} = \left. \frac{\partial S}{\partial N} \right|_{E,V} = k \ln \left\{ \frac{V}{N} \left(\frac{2E}{\sqrt{3}Nhc} \right)^3 \right\}$$

The heat capacity at a constant volume results as

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = 3Nk$$

Proof of Equation (6.53)

Equation (6.53) can be easily seen in the following way: Arbitrary sections of the n-dimensional cone with the hypersurfaces $x_n = \text{const.}$ are similar to the basis area. According to the theorem of Cavalieri the total volume is therefore given by

$$\text{Vol}_n = \int_0^h dx_n \text{area}(x_n) \tag{6.57}$$

The area at the height x_n can be easily calculated from the basis area. Namely, in the case of similarity mappings $\vec{r} \to \alpha\vec{r}$ for arbitrary volumes in n dimensions,

$$I_n(\alpha\vec{r}) = \alpha^n I_n(\vec{r}) \tag{6.58}$$

is valid. This formula is immediately understood in the case of a sphere in n dimensions with radius α. In our case, for the similar areas with $n-1$ dimensions it is therefore

$$\text{area}(x_n) = \text{area}(0)\left(1 - \frac{x_n}{h}\right)^{n-1}$$

where $1 - x_n/h$ is the *stretching factor* α in Equation (6.58). In the apex $x_n = h$, one has of course $F = 0$. Inserting this into Equation (6.57) yields

$$\text{Vol}_n = \text{area}(0)\int_0^h dx_n \left(1 - \frac{x_n}{h}\right)^{n-1} = \frac{h}{n}\,\text{area}(0)$$

if the integral is solved by the substitution $y = 1 - x_n/h$.

Exercise 6.3: Harmonic oscillators

Calculate the thermodynamic properties of a system of N classical *distinguishable* harmonic oscillators with frequency ω in the microcanonical ensemble.

Solution Analogously to the preceding example we first calculate (the oscillators are one-dimensional objects)

$$\Sigma(E, V, N) = \frac{1}{h^N}\int_{H(q_\nu, p_\nu)\le E} d^N q\, d^N p \tag{6.59}$$

Because of the distinguishability of the oscillators, in this case the Gibbs correction factor $1/N!$ must not be added. The distinguishability of the oscillators is in practice ensured, e.g., by localization at certain points in coordinate space.

The Hamiltonian of this system reads

$$H(q_\nu, p_\nu) = \sum_{\nu=1}^{N} \frac{p_\nu^2}{2m} + \frac{1}{2}m\omega^2 q_\nu^2$$

With the substitution $x_\nu = m\omega q_\nu$, Equation (6.59) becomes

$$\Sigma(E, V, N) = \frac{1}{h^N}\left(\frac{1}{m\omega}\right)^N \int_{\sum_{\nu=1}^{N}(p_\nu^2 + x_\nu^2)\le 2mE} d^N x\, d^N p$$

The integral corresponds exactly to the volume of a $2N$-dimensional sphere of radius $\sqrt{2mE}$, which we can calculate immediately, using Equation (5.30):

$$\Sigma(E, V, N) = \frac{1}{h^N}\left(\frac{1}{m\omega}\right)^N \frac{\pi^N}{N\Gamma(N)}(2mE)^N = \frac{1}{N\Gamma(N)}\left(\frac{E}{\hbar\omega}\right)^N \tag{6.60}$$

This yields $g(E, V, N)$, by differentiation with respect to energy,

$$g(E, V, N) = \left(\frac{1}{\hbar\omega}\right)^N \frac{E^{N-1}}{\Gamma(N)} \tag{6.61}$$

Therefore, using $\Omega \approx gE$, as well as $\ln\Gamma(N) = \ln(N-1)! \approx (N-1)\ln(N-1) - (N-1) \approx N\ln N - N$, since $N \gg 1$, the entropy is given by:

$$S(E, V, N) = Nk\left[1 + \ln\left\{\frac{E}{N\hbar\omega}\right\}\right] \tag{6.62}$$

This result is very interesting. Here we have considered classical oscillators and Equations (6.60) and (6.62) are *not* quantum mechanical results! Only the choice of the unique volume h^N in phase space leads here to the typical quantum mechanical combination $\hbar\omega$.

The thermodynamic properties of the system of N oscillators depend on the typical parameter $E/(N\hbar\omega)$, which measures the ratio between energy per particle and typical oscillator energy $\hbar\omega$. It is characteristic for many systems that the thermodynamic properties depend on the ratio of the total energy E and an energy which is characteristic for the system (in this case $\hbar\omega$).

With the aid of Equation (6.62), the equations of state can be easily calculated:

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = Nk\frac{1}{E}$$

$$E = NkT$$

$$\frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} = 0$$

$$p = 0$$

This is not very surprising, since the oscillators are fixed in space and have no free motion which could create a pressure. Hence, Ω and thus S do not depend on the volume of the container.

The chemical potential of the system is

$$-\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_{E,V} = k \ln\left\{\frac{E}{N\hbar\omega}\right\}$$

while the heat capacities

$$C = \frac{\partial E}{\partial T} = Nk \tag{6.63}$$

at constant volume or constant pressure have the same value, because the system cannot perform any volume work.

7 The Canonical Ensemble

The microcanonical ensemble is especially suited for closed systems with the natural variables E, V, and N. Since any system can be made into a total closed system by including its surroundings, the microcanonical ensemble in principle is suitable for describing any physical situation. It can, for instance, describe a system at temperature T, if the heat bath, or thermal reservoir, which fixes the temperature in the system is included in the total closed system. However, since in most cases the properties of such a heat bath do not interest us, this would be of no use. In addition, the microcanonical ensemble contains considerable mathematical difficulties, since the volumes of complicated high-dimensional geometric bodies have to be determined. Only in the most simple cases is this really possible (spheres, ashlars, simplices, etc.).

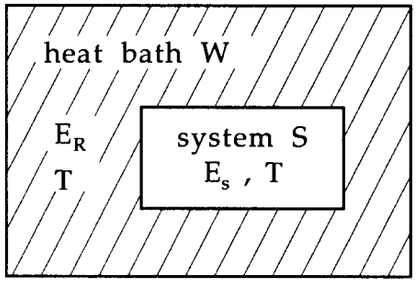


Figure 7.1. System in a heat bath.

Therefore we now want to reflect on the probability distribution (phase-space density) of a system at a given temperature (a system S in a heat bath R). To do this, we apply what we have learned up to now about the total closed system (heat bath plus system). The total energy of the whole system

$$E = E_R + E_S \tag{7.1}$$

has a constant given value.

By definition, the heat bath is very large compared to the system itself, so that

$$\frac{E_S}{E} = \left(1 - \frac{E_R}{E}\right) \ll 1 \tag{7.2}$$

Since now it is no longer the energy E_S which is fixed, but the temperature, the system S will be able to assume all possible microstates i with different energies E_i with a certain probability distribution. However, we expect that microstates with very large E_i will appear only very scarcely. We ask for the probability p_i of finding the system S in a certain microstate i with the energy E_i.

If S is a closed system, p_i will be proportional to the number of microstates $\Omega_S(E_i)$. Analogously, p_i is proportional to the number of microstates in the total closed system for which S lies in the microstate i with the energy E_i. Obviously this is just equal to the number of microstates of the heat bath for the energy $E - E_i$, since S only assumes one microstate i:

$$p_i \propto \Omega_R(E_R) = \Omega_R(E - E_i) \tag{7.3}$$

If the heat bath is very large, we can assume, according to Equation (7.2), that $E_i \ll E$, and we can expand Ω_R with respect to E_i. To be able to identify the derivates which occur in this procedure, we first expand $k \ln \Omega_R$, i.e., the entropy S_R of the heat bath,

$$k \ln \Omega_R(E - E_i) \approx k \ln \Omega_R(E) - \frac{\partial}{\partial E} (k \ln \Omega_R(E)) E_i + \cdots \tag{7.4}$$

For a very large heat bath the first two terms in Equation (7.4) are sufficient, since then we have $E \approx E_R \gg E_i$. However,

$$\frac{\partial}{\partial E} (k \ln \Omega_R(E)) = \frac{\partial S_R}{\partial E} = \frac{1}{T} \tag{7.5}$$

Insertion of Equation (7.5) into Equation (7.4) and exponentiation yields

$$\Omega_R(E - E_i) \approx \Omega_R(E) \exp\left\{-\frac{E_i}{kT}\right\} \tag{7.6}$$

The number of microstates of the heat bath thus decreases exponentially with the energy of the system. Since $E = \text{const}$, $\Omega_R(E)$ is a constant, and the probability p_i reads

$$p_i \propto \exp\left\{-\frac{E_i}{kT}\right\} \tag{7.7}$$

Here again, all microstates with the same energy E_i have the same probability, only now the energy is no longer fixed, but for a fixed temperature the system S can be on any of the possible energy surfaces. However, the probability now decreases with increasing E_i. Finally, p_i can be normalized to 1, so that $\sum_i p_i = 1$:

$$p_i = \frac{\exp\left\{-\frac{E_i}{kT}\right\}}{\sum_i \exp\left\{-\frac{E_i}{kT}\right\}} \tag{7.8}$$

Here the sum $\sum_i$ extends over all microstates (phase-space points). In continuous notation Equation (7.8) reads ($i \to (q_\nu, p_\nu)$ and $\sum_i \to 1/h^{3N} \int d^{3N}q\, d^{3N}p$):

$$\rho_c(q_\nu, p_\nu) = \frac{\exp\{-\beta H(q_\nu, p_\nu)\}}{\frac{1}{h^{3N}} \int d^{3N}q\, d^{3N}p \exp\{-\beta H(q_\nu, p_\nu)\}} \tag{7.9}$$

Here we have abbreviated the frequently appearing factor $1/kT$ by β. Equations (7.8) and (7.9) yield the *canonical phase-space density*, which we denote by the index c.

Because of its great importance, we want to derive the phase-space density once again in another way, using the language of ensemble theory.

In the canonical ensemble the energy E_i of the system is not fixed. Therefore, all phase-space points can be occupied (bear in mind that the ideal heat bath provides an infinitely

large energy reservoir). We subdivide the total phase space into equi-sized enumerated cells $\Delta\omega_i$. If these cells are sufficiently small, each of them will correspond to exactly one microstate i. We consider an ensemble of $\mathcal{N}$ identical systems (again, $\mathcal{N}$ must not be confused with the particle number N in the system). Each of these systems is in some microstate at a fixed time. Let there be just n_i systems in each phase-space cell $\Delta\omega_i$. Then it must hold that

$$\mathcal{N} = \sum_i n_i \tag{7.10}$$

where the sum extends over all phase-space cells. Just as in the microcanonical case, $p_i = n_i/\mathcal{N}$ is the probability that the microstate i appears in the ensemble of $\mathcal{N}$ systems. Now in the case of a system at a constant temperature, indeed all possible microstates i and thus all possible energies E_i can be assumed with the probability p_i, but of course *in equilibrium a certain mean value of energy* will be established, which we want to denote by U. The quantity U must emerge as a statistical mean value of all energies E_i which are actually assumed in the ensemble,

$$U = \langle E_i \rangle = \sum_i p_i E_i \tag{7.11}$$

or, with $p_i = n_i/\mathcal{N}$,

$$\mathcal{N}U = \sum_i n_i E_i \tag{7.12}$$

In addition to Equation (7.10), Equation (7.12) is thus another condition for the distribution $\{n_i\}$. Now a distribution of the systems $\{n_i\}$ over the phase-space cells $\Delta\omega_i$ can be achieved in many different ways, as we have already seen in the microcanonical case. However, now we do not deal with surface elements on the energy surface, but with the phase-space elements $\Delta\omega_i$ in the total phase space. The probability of the distribution $\{n_i\}$ in the microcanonical case is

$$W\{n_i\} = \mathcal{N}! \prod_i \frac{(\omega_i)^{n_i}}{n_i!} \tag{7.13}$$

Again, ω_i is the probability of finding *one* microstate within the cell $\Delta\omega_i$. Just as in the microcanonical case, we again look for the *most probable* distribution $\{n_i\}^*$ of the systems over the phase-space cells. But in this extreme value problem for $W\{n_i\}$ we now have two boundary conditions for the $\{n_i\}$, namely Equations (7.10) and (7.12). At first we form the logarithm of Equation (7.13), to remove the disturbing factors using Stirling's formula,

$$\ln W\{n_i\} = \mathcal{N} \ln \mathcal{N} - \mathcal{N} - \sum_i \{(n_i \ln n_i - n_i) - n_i \ln \omega_i\} \tag{7.14}$$

For an extremum of $\ln W$ the total differential must vanish,

$$d \ln W\{n_i\} = -\sum_i \{\ln n_i - \ln \omega_i\}\, dn_i = 0 \tag{7.15}$$

If here all n_i were independent of each other, each single coefficient would vanish. However, we know already how to fulfill the constraints with the aid of Lagrange multipliers. We

form the differentials of Equations (7.10) and (7.12) and multiply these with the unknown factors λ and $-\beta$. (The minus sign here is arbitrary, but it will prove to be advantageous at the end of the calculation.)

$$\lambda \sum_i dn_i = 0 \tag{7.16}$$

$$-\beta \sum_i E_i \, dn_i = 0 \tag{7.17}$$

Equations (7.16) and (7.17) are now added to Equation (7.15):

$$\sum_i (\ln n_i - \ln \omega_i - \lambda + \beta E_i) \, dn_i = 0 \tag{7.18}$$

Now we can assume all dn_i to be independent of each other, and we can fulfill conditions (7.10) and (7.12) afterwards by a convenient choice of λ and β. Then each coefficient of Equation (7.18) must vanish,

$$\ln n_i = \lambda + \ln \omega_i - \beta E_i \qquad \text{or} \qquad n_i = \omega_i e^{\lambda} e^{-\beta E_i} \tag{7.19}$$

Equation (7.10) can be used to determine the factor e^{λ}. We make use of the fact that the elementary probabilities ω_i for equally large phase-space cells must be equal. This yields

$$p_i = \frac{n_i}{\mathcal{N}} = \frac{\exp\{-\beta E_i\}}{\sum_i \exp\{-\beta E_i\}} \tag{7.20}$$

We see that in this way we end up exactly with the form (7.8); only the factor β must still be determined from Equations (7.11) or (7.12),

$$U = \langle E_i \rangle = \frac{\sum_i E_i \exp\{-\beta E_i\}}{\sum_i \exp\{-\beta E_i\}} \tag{7.21}$$

This means, that if one fixes a certain mean energy U for the system, then according to Equation (7.21), the factor β is a function of U. Of course, comparing Equation (7.20) to Equation (7.8) we guess immediately that $\beta = 1/kT$. However, we want to identify β in a somewhat different way. To do so we first define the abbreviation

$$Z = \sum_i \exp\{-\beta E_i\} \tag{7.22}$$

The quantity Z is the so-called *canonical partition function* (the letter Z comes from the german word *Zustandssumme*), since the sum $\sum_i$ extends over all possible microstates. Now the entropy should result as the ensemble average of the quantity $-k \ln \rho_c$, thus written in continuous notation:

$$S = \langle -k \ln \rho_c \rangle = \frac{1}{h^{3N}} \int d^{3N}q \, d^{3N}p \rho_c(q_v, p_v)(-k \ln \rho_c(q_v, p_v)) \tag{7.23}$$

Now for the term $\rho_c(q_v, p_v)$ in the logarithm we insert p_i from Equation (7.20), and we again replace $\sum_i$ by $1/h^{3N} \int d^{3N}q \, d^{3N}p$, and E_i by $H(q_v, p_v)$ (as before, in the step between Equation (7.8) and (7.9)), but now with unknown β. The continuously written

partition function then reads

$$Z = \frac{1}{h^{3N}} \int d^{3N}q \, d^{3N}p \exp\{-\beta H(q_\nu, p_\nu)\} \tag{7.24}$$

and the p_i become

$$\rho_c(q_\nu, p_\nu) = \frac{\exp\{-\beta H(q_\nu, p_\nu)\}}{Z} \tag{7.25}$$

These $\rho_c(q_\nu, p_\nu)$ are, so to say, the *continuously written* p_i of Equation (7.20), just as Equations (7.8) and (7.9) are only a different manner of writing the same quantity. It follows for the entropy, according to Equation (7.23):

$$S = \frac{1}{h^{3N}} \int d^{3N}q \, d^{3N}p \rho_c(q_\nu, p_\nu) [k\beta H(q_\nu, p_\nu) + k \ln Z] \tag{7.26}$$

Now the first term in the square bracket (up to the coefficient $k\beta$) yields exactly the definition of the ensemble average of H, namely $\langle H \rangle$, while the second term ($\ln Z$) does not depend at all on the phase-space point (cf. Equation (7.24)) and may therefore be brought in front of the integral. Because of the normalization of phase-space density we therefore obtain for Equation (7.26):

$$S = k\beta \langle H \rangle + k \ln Z \tag{7.27}$$

The ensemble average of the energy $\langle H \rangle$ is, according to Equation (7.21), the mean energy U of the system, and instead of Equation (7.27) we have

$$S = k\beta U + k \ln Z \tag{7.28}$$

Now we form $\partial S/\partial U = 1/T$, where we must, however, take care of the fact that $\beta(U)$, as well as $k \ln Z(\beta(U))$, are functions of U. The mean energy U can, of course, be identified with the internal energy U, thus

$$\frac{1}{T} = \frac{\partial S}{\partial U} = kU \frac{\partial \beta}{\partial U} + k\beta + \frac{\partial}{\partial U}(k \ln Z) \tag{7.29}$$

Now one has

$$\frac{\partial}{\partial U}(k \ln Z) = \frac{\partial}{\partial \beta}(k \ln Z) \frac{\partial \beta}{\partial U} \tag{7.30}$$

because according to Equation (7.22) Z is a function of U only via β. Now we have

$$\frac{\partial}{\partial \beta}(k \ln Z) = \frac{k}{Z} \left(- \sum_i E_i \exp\{-\beta E_i\} \right) = -kU \tag{7.31}$$

so that Equation (7.29), using Equations (7.30) and (7.31), reduces to

$$\frac{\partial S}{\partial U} = \frac{1}{T} = k\beta \Rightarrow \beta = \frac{1}{kT} \tag{7.32}$$

Thus the Lagrange multiplier from Equation (7.17) is really $1/(kT)$, as we had already concluded from the comparison of Equation (7.20) with Equation (7.8). However, Equation

(7.28) is of great importance beyond the determination of β. If one rewrites it, using $\beta = 1/(kT)$, one obtains

$$U - TS = -kT \ln Z \tag{7.33}$$

We know from thermodynamics that

$$F(T, V, N) = U - TS \tag{7.34}$$

is the *free energy of the system.* So we have derived the following important statement:

$$F(T, V, N) = -kT \ln Z(T, V, N) \tag{7.35}$$

This relation in the canonical ensemble at a given temperature is completely analogous to the relation

$$S(E, V, N) = k \ln \Omega(E, V, N) \tag{7.36}$$

from the microcanonical ensemble. Just as in the latter case, the entropy, which is the thermodynamic potential of the closed system, can be calculated from the quantity Ω, now the free energy is to be calculated from the partition function Z. In Ω all accessible states of the energy surface for a given E are counted with equal weights. In the calculation of Z at a given energy for the system, again all accessible states of *one* energy surface are equally probable, but now there occur all different energy surfaces with a probability proportional to the so-called *Boltzmann factor* $e^{-\beta E}$. Just like the microcanonical phase-space density, the canonical density also depends only on $H(q_\nu, p_\nu)$, as it should, according to our considerations of Liouville's theorem.

Now we want to show via some examples that in the canonical ensemble all thermodynamic properties of the system also can be calculated from a given Hamiltonian. However, before we can do this, we still must reflect on how to build the Gibbs correction factor into the canonical ensemble.

General foundation of the Gibbs correction factor

In the microcanonical ensemble we have seen, considering Gibbs' paradox, that the classical enumerability of particles directly leads to a contradiction to thermodynamics. There we introduced a correction of the number of microstates $\Omega(E, V, N)$ by the factor $1/N!$:

$$\begin{aligned} \Omega_d(E, V, N) &= \int_{E \le H \le E+\Delta E} \frac{d^{3N}q\, d^{3N}p}{h^{3N}} \\ \rightarrow \Omega_{nd}(E, V, N) &= \int_{E \le H \le E+\Delta E} \frac{d^{3N}q\, d^{3N}p}{N!h^{3N}} \end{aligned} \tag{7.37}$$

Here the index d stands for distinguishable and nd for nondistinguishable particles. This correction can be directly taken over to arbitrary ensembles, if everywhere the infinitesimal

phase-space volumes are replaced accordingly,

$$d\Omega_d(E, V, N) = \frac{d^{3N}q\, d^{3N}p}{h^{3N}} \rightarrow d\Omega_{nd}(E, V, N) = \frac{d^{3N}q\, d^{3N}p}{N!h^{3N}} \tag{7.38}$$

In the case of the canonical ensemble the phase-space density is given by

$$\rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) = \frac{1}{Z(T, V, N)} \exp\{-\beta H(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)\} \tag{7.39}$$

The partition function $Z(T, V, N)$ is here, in analogy to the microcanonical case for distinguishable particles, given by

$$Z_d(T, V, N) = \int \frac{d^{3N}q\, d^{3N}p}{h^{3N}} \exp\{-\beta H\} \tag{7.40}$$

and for nondistinguishable particles, by

$$Z_{nd}(T, V, N) = \int \frac{d^{3N}q\, d^{3N}p}{N!h^{3N}} \exp\{-\beta H\} \tag{7.41}$$

Now we want to give a more detailed foundation of the generalizations (7.38), (7.40), and (7.41) for arbitrary ensembles. The phase-space density $\rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)$ for distinguishable particles denotes the probability density for particle 1 to be at $\vec{r}_1$ and to have the momentum $\vec{p}_1$, etc. This can be used to calculate the probability density for *any* particle to be at $\vec{r}_1$ with momentum $\vec{p}_1$, etc. One has only to sum up the probability densities for arbitrary renumberings of the particles:

$$\rho_{nd}(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) = \sum_P \rho_d(\vec{r}_{P1}, \ldots, \vec{r}_{PN}, \vec{p}_{P1}, \ldots, \vec{p}_{PN}) \tag{7.42}$$

The sum extends over all permutations $(P_1, \ldots, P_N)$ of $(1, \ldots, N)$. Now we require that the Hamiltonian of the system does not change for different enumerations of the particle coordinates and momenta. Then

$$H(\vec{r}_{P1}, \ldots, \vec{r}_{PN}, \vec{p}_{P1}, \ldots, \vec{p}_{PN}) = H(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) \tag{7.43}$$

is valid for all permutations. This immediately yields

$$\rho_d(\vec{r}_{P1}, \ldots, \vec{r}_{PN}, \vec{p}_{P1}, \ldots, \vec{p}_{PN}) = \rho_d(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) \tag{7.44}$$

because according to Equation (7.39) ρ_d depends on the $\vec{r}_i$ and $\vec{p}_i$ only via the Hamiltonian H. Equation (7.42) becomes (the sum now consists of $N!$ equal summands)

$$\rho_{nd}(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) = N!\rho_d(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) \tag{7.45}$$

One can see that there appears just the factor $N!$, which is also obtained if instead of $Z_d(T, V, N)$ the expression for $Z_{nd}(T, V, N)$ is inserted into Equation (7.39). Thus we have not only found the foundation for the generalization of the Gibbs correction factor to arbitrary ensembles, but with Equation (7.43) we also have a criterion on systems to which it may be applied. These are systems whose Hamiltonians are invariant under a different

enumeration of the coordinates and momenta. The Hamiltonian of the ideal gas,

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} = \sum_{i=1}^{N} \frac{\vec{p}_{Pi}^{\,2}}{2m} \tag{7.46}$$

fulfills this condition. Here in the last term the index P_i stands for an arbitrary permutation of the numbers i. However, one can also find examples where condition (7.43) is not fulfilled. This is the case, for instance, if one attaches to every particle an individual potential which explicitly depends on the particle number:

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i=1}^{N} \frac{1}{2} m\omega^2 \left(\vec{r}_i - \vec{b}_i\right)^2 \tag{7.47}$$

If here the enumeration of the coordinates is changed, in general the second sum changes, because the fixed vectors $\vec{b}_i$, which fix the respective zero points of the oscillator potential, are not renumbered. Observe that the probability

$$\begin{aligned} d^{6N}w &= \rho_d(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) \frac{d^{3N}q\, d^{3N}p}{h^{3N}} \\ &= \rho_{nd}(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) \frac{d^{3N}q\, d^{3N}p}{N!h^{3N}} \end{aligned} \tag{7.48}$$

of finding the total system in any phase-space cell $d^{3N}q\, d^{3N}p$, is the same in both cases, since the factor $N!$ from the phase-space density cancels the factor $N!$ from the volume element. This is simply a consequence of the normalization $\int d^{6N}w = 1$.

Example 7.1: The Ideal Gas in the Canonical Ensemble

It follows from our considerations in the preceding section that for a system in a heat bath it is sufficient to calculate the partition function: this yields the free energy, from which follows all properties of the system at a given temperature, just as all properties of a closed system can be calculated from the entropy.

The Hamiltonian of the ideal gas is

$$H(q_\nu, p_\nu) = \sum_{\nu=1}^{3N} \frac{p_\nu^2}{2m}$$

if the momenta are enumerated from 1 to $3N$. The definition of the partition function with the Gibbs' factor reads

$$Z(T, V, N) = \frac{1}{N!h^{3N}} \int d^{3N}q\, d^{3N}p \exp\{-\beta H(q_\nu, p_\nu)\}$$

Since for the ideal gas H does not depend on the coordinates, the integral $\int d^{3N}q$ simply yields the factor V^N, if V is the volume of the container. Because of the exponential function, the momentum integrals factor,

$$Z(T, V, N) = \frac{1}{N!h^{3N}} V^N \prod_{\nu=1}^{3N} \int_{-\infty}^{+\infty} dp_\nu \exp\left\{-\beta \frac{p_\nu^2}{2m}\right\}$$

With the substitution $x = \sqrt{\beta/2m}\,p_\nu$, all these integrals can be reduced to the same standard integral

$$\int_{-\infty}^{+\infty} dx e^{-x^2} = \sqrt{\pi}$$

and the result reads

$$Z(T, V, N) = \frac{V^N}{N!h^{3N}} \left(\frac{2m\pi}{\beta}\right)^{3N/2} = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \tag{7.49}$$

As we can see, the calculation of the partition function of the ideal gas at a given temperature is much easier than the analogous calculation in the microcanonical ensemble. The reason is that for a system of *noninteracting* particles (the Hamiltonian of which is the sum of one-particle Hamiltonians) the exponential factor in the integral always factors, resulting in a considerable simplification. The result (7.49) can again be rewritten for the already well-known thermal wavelength,

$$\lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$

leading to

$$Z(T, V, N) = \frac{V^N}{N!\lambda^{3N}} \tag{7.50}$$

Therewith we also know the free energy

$$F(T, V, N) = -kT \ln Z(T, V, N) = -NkT \left(1 + \ln\left\{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\}\right) \tag{7.51}$$

if Stirling's formula is used for $\ln N!$. From the free energy we can again calculate all thermodynamic properties. For instance, we have

$$\begin{aligned} p &= -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{NkT}{V} \qquad \text{or} \qquad pV = NkT \\ S &= -\left.\frac{\partial F}{\partial T}\right|_{V,N} = Nk\left[\frac{5}{2} + \ln\left\{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\}\right] \\ \mu &= \left.\frac{\partial F}{\partial N}\right|_{T,V} = -kT \ln\left\{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} \end{aligned} \tag{7.52}$$

First we obtain all quantities as functions of T, V, N. Now using Equations (7.51) and (7.52) we can calculate

$$U = F + TS = \frac{3}{2}NkT$$

This can, for instance, be used to replace the temperature by the internal energy, so that we obtain

$$S(U, V, N) = Nk\left[\frac{5}{2} + \ln\left\{\frac{V}{N}\left(\frac{4\pi mU}{3h^2N}\right)^{3/2}\right\}\right]$$

The results are completely identical to the results in the case of the microcanonical ensemble! This is to be expected, since the free energy (canonical ensemble) and the entropy (microcanonical ensemble) are equivalent thermodynamic potentials, which evolve from each other by a Legendre transformation.

Exercise 7.2: The ultrarelativistic gas

Calculate the thermodynamic properties of the ultrarelativistic gas (cf. Example 6.2) in the canonical ensemble.

Solution

We start with the Hamiltonian

$$H(q_\nu, p_\nu) = \sum_{\nu=1}^{N} |\vec{p}_\nu| c$$

and calculate the partition function (with the Gibbs' factor, since the particles, as in the case of the ideal gas, are indistiguishable),

$$Z(T, V, N) = \frac{1}{N! h^{3N}} \int d^{3N}q \, d^{3N}p \exp\{-\beta H(q_\nu, p_\nu)\}$$

As in the preceding example, the Hamiltonian does not depend on the coordinates, so the coordinate-space integral yields V^N. Again the remaining integrals factor,

$$Z(T, V, N) = \frac{1}{N! h^{3N}} V^N \prod_{\nu=1}^{N} \int d^3 p_\nu \exp\{-\beta |\vec{p}_\nu| c\}$$

It is convenient to transform to spherical polar coordinates in each integral. This leads to

$$Z(T, V, N) = \frac{V^N}{N! h^{3N}} \left(4\pi \int_0^\infty p^2 \, dp e^{-\beta c p}\right)^N$$

Using the substitution $\beta c p = x$, the remaining integral can be reduced to the Γ-function,

$$\int_0^\infty p^2 \, dp e^{-\beta c p} = \left(\frac{1}{\beta c}\right)^3 \int_0^\infty x^2 \, dx e^{-x} = \left(\frac{1}{\beta c}\right)^3 \Gamma(3)$$

where $\Gamma(3)$, according to $\Gamma(n+1) = n!$, simply yields the factor 2:

$$Z(T, V, N) = \frac{V^N}{N! h^{3N}} \left(8\pi \left(\frac{1}{\beta c}\right)^3\right)^N = \frac{1}{N!} \left(8\pi V \left(\frac{kT}{hc}\right)^3\right)^N$$

The free energy is calculated, using Stirling's formula for $\ln N!$:

$$F(T, V, N) = -kT \ln Z(T, V, N) = -NkT \left[1 + \ln\left\{\frac{8\pi V}{N} \left(\frac{kT}{hc}\right)^3\right\}\right]$$

This can again be used to derive the equations of state of the ultrarelativistic gas:

$$p = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{NkT}{V} \qquad \text{or} \qquad pV = NkT$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = Nk \left[4 + \ln\left\{\frac{8\pi V}{N} \left(\frac{kT}{hc}\right)^3\right\}\right]$$

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = -kT \ln\left\{\frac{8\pi V}{N}\left(\frac{kT}{hc}\right)^3\right\}$$

As we can see, in this case the term $(8\pi)^{1/3}hc/(kT)$ takes the role of the thermal wavelength of the ideal gas. To enable a comparison with the microcanonical calculation, we calculate the internal energy,

$$U = F + TS = 3NkT$$

This can be used to substitute the energy per particle for the temperature. For instance, one has

$$S(U, V, N) = Nk\left[4 + \ln\left\{\frac{8\pi V}{N}\left(\frac{U}{3Nhc}\right)^3\right\}\right]$$

This exact result does not completely coincide with Equation (6.54). There the factor $(2/\sqrt{3})^3 \approx 1.539$ appeared instead of the factor $8\pi/27 \approx 0.931$ in the logarithm. Recall, however, that there the aproximation $\sqrt{3}|\vec{p}| \approx |p_x| + |p_y| + |p_z|$ had been used. Therefore, the difference of the results neither reflects a mistake in our calculation nor even a principal problem.

Exercise 7.3: Harmonic oscillators in the canonical ensemble

Calculate the thermodynamic properties of a set of N distinguishable harmonic oscillators of frequency ω.

Solution The Hamiltonian for this system reads

$$H(q_\nu, p_\nu) = \sum_{\nu=1}^{N}\left(\frac{p_\nu^2}{2m} + \frac{1}{2}m\omega^2 q_\nu^2\right)$$

This must now be used to calculate the partition function (without the Gibbs' factor)

$$Z(T, V, N) = \frac{1}{h^N}\int d^N q\, d^N p \exp\{-\beta H(q_\nu, p_\nu)\}$$

Here all integrals factor, too, since H is only a sum of one-particle Hamiltonians,

$$Z(T, V, N) = \frac{1}{h^N}\prod_{\nu=1}^{N}\left[\int_{-\infty}^{+\infty} dq_\nu \exp\left\{-\beta\frac{1}{2}m\omega^2 q_\nu^2\right\} \times \int_{-\infty}^{+\infty} dp_\nu \exp\left\{-\beta\frac{p_\nu^2}{2m}\right\}\right]$$

Using the substitutions $\sqrt{\beta m\omega^2/2}q_\nu = x$ and $\sqrt{\beta/2m}p_\nu = y$, the integrals become Gaussian integrals. The result of the integration is

$$Z(T, V, N) = \frac{1}{h^N}\left[\left(\frac{2\pi}{\beta m\omega^2}\right)^{1/2}\left(\frac{2m\pi}{\beta}\right)^{1/2}\right]^N$$

$$Z(T, V, N) = \left(\frac{kT}{\hbar\omega}\right)^N$$

with $\hbar = h/2\pi$. For the free energy this implies

$$F(T, V, N) = -kT \ln Z(T, V, N) = -NkT \ln\left\{\frac{kT}{\hbar\omega}\right\}$$

Therewith the thermodynamic equations of state follow as

$$p = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = 0$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = Nk\left[1 + \ln\left\{\frac{kT}{\hbar\omega}\right\}\right]$$

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = -kT \ln\left\{\frac{kT}{\hbar\omega}\right\}$$

The internal energy is

$$U = F + TS = NkT$$

Thus $S(U, V, N)$ reads

$$S(U, V, N) = Nk\left[1 + \ln\left\{\frac{E}{N\hbar\omega}\right\}\right]$$

which coincides exactly with the microcanonical calculation. The equations of state are also identical.

Systems of noninteracting particles

In the preceding examples and exercises we have seen that the calculation of systems for which the Hamiltonian is a sum of one-particle Hamiltonians,

$$H(q_1, \ldots, q_{3N}, p_1, \ldots, p_{3N}) = \sum_{\nu=1}^{N} h(q_\nu, p_\nu) \tag{7.53}$$

is especially easy in the canonical ensemble. Let h be a one-particle Hamiltonian, which depends *only* on the variables q_ν and p_ν of the νth particle (e.g., $p_\nu^2/2m$). Now the partition function reads (with the Gibbs' factor)

$$\begin{aligned} Z(T, V, N) &= \frac{1}{N!h^{3N}} \int d^{3N}q\, d^{3N}p \exp\{-\beta H(q_\nu, p_\nu)\} \\ &= \frac{1}{N!h^{3N}} \prod_{\nu=1}^{N} \int d^3q_\nu\, d^3p_\nu \exp\{-\beta h(q_\nu, p_\nu)\} \end{aligned} \tag{7.54}$$

The integral can be interpreted as a one-particle partition function ($N = 1$),

$$Z(T, V, 1) = \frac{1}{h^3} \int d^3q\, d^3p \exp\{-\beta h(q, p)\} \tag{7.55}$$

so that the partition function of the N-particle system can be directly calculated from that of the one-particle system;

$$Z(T, V, N) = \frac{1}{N!} (Z(T, V, 1))^N \tag{7.56}$$

for nondistinguishable particles, and

$$Z(T, V, N) = (Z(T, V, 1))^N \tag{7.57}$$

for distinguishable particles, respectively. This is a very useful prescription of calculation, since in this case one effectively deals with one-particle problems. Let us now consider the phase-space density of the total system,

$$\begin{aligned}\rho_N &= \frac{\exp\{-\beta H(q_\nu, p_\nu)\}}{Z(T, V, N)} \\ &= N! \left(\frac{\exp\{-\beta h(q_1, p_1)\}}{Z(T, V, 1)}\right)\left(\frac{\exp\{-\beta h(q_2, p_2)\}}{Z(T, V, 1)}\right)\cdots\end{aligned} \tag{7.58}$$

Up to the Gibbs factor, the probability $\rho_N(q_\nu, p_\nu)$ of finding the N particles exactly at the phase-space point $(\vec{q}, \vec{p})$ equals the product of all probabilities of finding a certain particle in a certain one-particle microstate.

Obviously, for a system of noninteracting particles, the probability of finding a particle at the coordinate q with the momentum p, is just given by the distribution

$$\rho_1(q, p) = \frac{\exp\{-\beta h(q, p)\}}{Z(T, V, 1)} \tag{7.59}$$

Note that this is not self-evident. Originally Equation (7.59) was the distribution for a system which contains only *one* particle in all. Since the N particles in a noninteracting system do not influence each other, Equation (7.59) is at the same time the correct one-particle phase-space density for such a many-particle system. Therefore we can interpret such a system as an ideal ensemble. Each individual of the N particles forms a "system" by itself and at a given time occupies a certain one-particle microstate. All the other particles of the system form the heat bath at a given temperature.

It is crucial for these considerations that the probability of finding a particle in a certain microstate is independent of the microstates of the other particles: in ensemble theory the single systems of an ensemble are independent of each other. In an interacting system this is no longer true. Then the microstate of a certain particle depends on those of all other particles. The Hamiltonian for a special particle then also contains the coordinates and momenta of all other particles, and we cannot write down an equation corresponding to Equation (7.59).

Example 7.4: The ideal gas

As an example, we again consider the ideal gas,

$$H(\vec{q}_i, \vec{p}_i) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \Rightarrow h(q, p) = \frac{\vec{p}^{\,2}}{2m}$$

The probability density for finding any particle in the one-particle phase space with the coordinate $\vec{q}$ and the momentum $\vec{p}$, is given by

$$\rho(q, p) = \frac{\exp\{-\beta h(q, p)\}}{Z(T, V, 1)} = \frac{\lambda^3}{V} \exp\left\{-\frac{\beta}{2m}\vec{p}^2\right\}$$

with $Z(T, V, 1) = V/\lambda^3$, according to Equation (7.50).

Now we are able to check the velocity distribution in the gas, which we had already derived earlier in Example 1.2. The probability of finding a particle with a coordinate between $\vec{q}$ and $\vec{q} + d\vec{q}$ and a momentum between $\vec{p}$ and $\vec{p} + d\vec{p}$ is $\rho\, d^3q\, d^3p/h^3$. For the velocity distribution $f(\vec{v})$ this implies

$$f(\vec{v})d^3v = \frac{m^3}{h^3} d^3v \int d^3q \frac{\lambda^3}{V} \exp\left\{-\frac{1}{2}\beta m\vec{v}^2\right\}$$

if $\vec{p} = m\vec{v}$ is inserted and if one integrates over all coordinates. The integral $\int d^3q$ just yields the volume V; this leads to

$$f(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\frac{m\vec{v}^2}{2kT}\right\}$$

Indeed, this coincides with Equation (1.13). Recall that the factor $1/h^3$ appears because ρ is a dimensionless quantity and the phase-space volumes are measured in units of h^{3N} (here N=1). This example is well suited to demonstrate, once again, the significance of the Gibbs factor in a very beautiful way. One has

$$\rho'(\vec{q}_1, \vec{q}_2, \ldots, \vec{p}_1, \vec{p}_2, \ldots) = \rho(\vec{q}_1, \vec{p}_1)\rho(\vec{q}_2, \vec{p}_2) \cdots \rho(\vec{q}_N, \vec{p}_N) \qquad \textbf{(7.60)}$$

with $\rho'(\vec{q}_i, \vec{p}_i)$ being the probability density of finding particle 1 in microstate $\vec{q}_1$, $\vec{p}_1$ *and* particle 2 in microstate $\vec{q}_2$, $\vec{p}_2$ *and* ... *and* particle N in $\vec{q}_N$, $\vec{p}_N$. However, this is true only for a given enumeration of the particles. If one asks for the probability of finding *any* of the N particles in $\vec{q}_1$, $\vec{p}_1$ and *any* in $\vec{q}_2$, $\vec{p}_2$ etc., then Equation (7.60) must be multiplied by the number of all ways of enumerating them in a different way, namely $N!$.

Exercise 7.5: Mean velocity and most probable velocity

Calculate the most probable, the mean, and the root mean square absolute velocity in the ideal gas, using the velocity distribution

$$f(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\beta\frac{1}{2}m\vec{v}^2\right\}$$

Solution The differential

$$d^3w(\vec{v}) = f(\vec{v})d^3\vec{v} \qquad \textbf{(7.61)}$$

denotes the probability of finding a particle in the ideal gas with the velocity vector $\vec{v}$ between (v_x, v_y, v_z) and $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$, independent of its position. At first we use this to calculate the probability of finding a particle which has an absolute value of velocity between $|\vec{v}|$ and $|\vec{v}| + |d\vec{v}|$. To do so, in Equation (7.61) one simply substitutes polar coordinates for the velocity vector and integrates over all spatial directions:

$$dw(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\beta\frac{1}{2}mv^2\right\} 4\pi v^2\, dv \qquad \textbf{(7.62)}$$

Equation (7.62) is Maxwell's velocity distribution for an ideal gas. The most probable absolute value of the velocity, v^*, corresponds to the maximum of the function $F(v) = dw/dv$. The latter is calculated from

$$F'(v)|_{v^*} = 0$$

$$\Leftrightarrow 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left[-\frac{m}{kT} \exp\left\{-\frac{mv^2}{2kT}\right\} v^3 + \exp\left\{-\frac{mv^2}{2kT}\right\} 2v\right]_{v^*} = 0$$

$$\Rightarrow -\frac{m}{2kT}(v^*)^3 + v^* = 0$$

$$\Rightarrow v^* = \sqrt{\frac{2kT}{m}}$$

The mean absolute value of velocity $\langle|\vec{v}|\rangle$ is defined as

$$\langle|\vec{v}|\rangle = \int_0^\infty F(v) v \, dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty \exp\left\{-\frac{mv^2}{2kT}\right\} v^3 \, dv \qquad \textbf{(7.63)}$$

Using the substitution $y = mv^2/2kT$, one can reduce the integral to the Γ-function (cf. Example 1.2):

$$\langle v\rangle = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2kT}{m}\right)^2 \frac{1}{2} \int_0^\infty e^{-y} y \, dy$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2kT}{m}\right)^2 \frac{1}{2} \Gamma(2)$$

Using $\Gamma(2) = 1$ yields after arranging

$$\langle v\rangle = \sqrt{\frac{8kT}{m\pi}} \qquad \textbf{(7.64)}$$

The mean squared velocity is calculated in a very similar way:

$$\langle v^2\rangle = \int_0^\infty F(v) v^2 \, dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty \exp\left\{-\frac{mv^2}{2kT}\right\} v^4 \, dv$$

Using the same substitution as in Equation (7.63), one obtains

$$\langle v^2\rangle = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2kT}{m}\right)^{5/2} \frac{1}{2} \int_0^\infty e^{-y} y^{3/2} \, dy$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2kT}{m}\right)^{5/2} \frac{1}{2} \frac{3}{4} \sqrt{\pi}$$

because $\Gamma(5/2) = (3/2)\Gamma(3/2) = (3/2)(1/2)\sqrt{\pi}$. This yields

$$\langle v^2\rangle = \frac{3kT}{m} \qquad \text{and} \qquad \sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}}$$

Maxwell's velocity distribution is depicted in Figure 7.2. The most probable velocity has been normalized to 1 by the choice of the units on the abscissa. As one can see, $v^* < \langle v\rangle < \sqrt{\langle v^2\rangle}$. All three velocities are essentially determined by the ratio kT/m. The mean kinetic energy of a particle follows as

$$\langle \epsilon_{kin}\rangle = \frac{1}{2} m \langle v^2\rangle = \frac{3}{2} kT$$

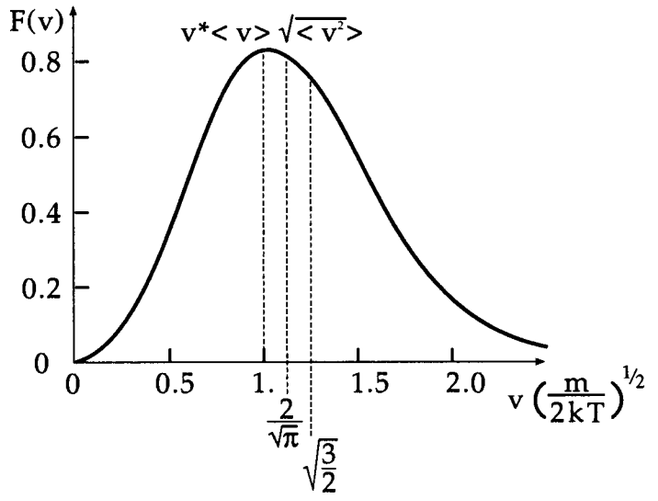


Figure 7.2. Maxwell's velocity distribution.

in coincidence with our result (1.9). Because of the isotropy of the distribution $f(\vec{v})$ we have, furthermore, that

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle = \frac{kT}{m}$$

Exercise 7.6: Velocity distribution of an evaporating gas

Calculate the velocity distribution $f^*(v)$ of particles evaporating from a hole in a container with an ideal gas at temperature T (Figure 7.3).

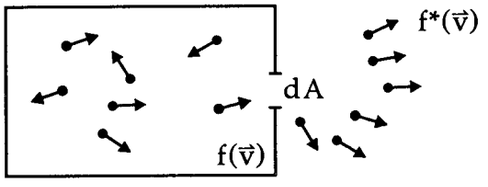


Figure 7.3. The system.

Assume that the equilibrium in the interior of the container is not disturbed by the evaporating particles. In addition, calculate the mean velocity in z-direction and the mean squared velocity of the evaporating particles, as well as the rate $R = d^2N/dt\,dA$ of the particles leaving the container per unit time and hole area.

Show that in general $R = \frac{1}{4}(N/V)\langle v \rangle$, if $\langle v \rangle$ is the mean absolute value of the velocity in the interior. What force acts on the container due to momentum conservation?

Solution

At first it is clear that each particle which hits the surface element dA from the interior leaves the container with the same velocity. In Chapter 1, Equation (1.5), we obtained by a simple consideration the number d^5N of particles, which in the time dt hit a surface element dA of the container wall with a velocity vector $\vec{v}$. We have

$$d^5N = \frac{N}{V} v_z\, dt\, dA f(\vec{v}) d^3\vec{v} \tag{7.65}$$

if the z-direction is chosen perpendicular to the surface element dA and if $f(\vec{v})$ is the velocity distribution in the gas. This holds only for $v_z > 0$, because particles with $v_z < 0$ move in the wrong direction.

Now one easily understands that the velocity distribution $f^*(\vec{v})$ of the particles which leave the container must be proportional to $v_z f(\vec{v})$,

$$f^*(\vec{v}) = c v_z f(\vec{v}) \tag{7.66}$$

For, if a particle had $v_z = 0$, it would not leave the container at all, $f^*(\vec{v})|_{v_z=0} = 0$. We have already included in Equation (7.66) the assumption that the equilibrium in the interior of the container is not essentially disturbed by the particles leaving the container.

The constant of proportionality c is determined by the normalization

$$\int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y \int_{-\infty}^{+\infty} dv_z f^*(\vec{v}) = 1 \tag{7.67}$$

To simplify the following calculations, we write the Maxwell distribution $f(\vec{v})$ in the form

$$f(\vec{v}) = f_x(v_x) f_y(v_y) f_z(v_z)$$

with the distributions of the single velocity components

$$f_i(v_i) = \sqrt{\frac{m}{2\pi kT}} \exp\left\{-\frac{mv_i^2}{2kT}\right\}$$

which are separately normalized to 1. The velocities of the particles leaving in the x- and y-directions have the same Gaussian distribution as in the interior of the container, while the z-component has been weighted by an additional factor $v_z > 0$. Equation (7.67) becomes

$$c \int_0^{\infty} dv_z v_z f_z(v_z) = 1$$

or

$$c\sqrt{\frac{m}{2\pi kT}} \int_0^{\infty} dv_z v_z \exp\left\{-\frac{mv_z^2}{2kT}\right\} = 1$$

With the usual substitution $y = mv_z^2/2kT$, one obtains

$$c\sqrt{\frac{m}{2\pi kT}} \frac{kT}{m} \int_0^{\infty} e^{-y}\, dy = 1 \Rightarrow c = \sqrt{\frac{2\pi m}{kT}}$$

The normalized velocity distribution of the particles which leave the container is

$$f^*(\vec{v}) = f_x(v_x) f_y(v_y) \sqrt{\frac{2\pi m}{kT}}\, v_z f_z(v_z)$$

This yields the mean velocity of the particles in the z-direction:

$$\begin{aligned}
\langle v_z \rangle^* &= \int v_z f^*(\vec{v})\, d^3\vec{v} = \sqrt{\frac{2\pi m}{kT}} \int_0^{\infty} v_z^2 f_z(v_z)\, dv_z \\
&= \frac{m}{kT} \int_0^{\infty} v_z^2 \exp\left\{-\frac{mv_z^2}{2kT}\right\} dv_z \\
&= \frac{m}{kT} \frac{kT}{m} \sqrt{\frac{2kT}{m}} \int_0^{\infty} y^{1/2} e^{-y}\, dy = \sqrt{\frac{2kT}{m}}\, \Gamma\left(\frac{3}{2}\right)
\end{aligned}$$

The asterisk at the mean value bracket indicates that one has to take the mean value using the distribution f^*. Because $\Gamma(3/2) = \sqrt{\pi}/2$ we obtain

$$\langle v_z \rangle^* = \sqrt{\frac{\pi kT}{2m}}$$

Of course, here one has a positive mean value for the component v_z. In the container itself, on the other hand, one has $\langle v_z \rangle = 0$. Analogously, the mean squared velocity in the z-direction

is given by

$$\langle v_z^2 \rangle^* = \int v_z^2 f^*(\vec{v})\, d^3\vec{v} = \sqrt{\frac{2\pi m}{kT}} \int_0^\infty v_z^3 f_z(v_z)\, dv_z$$

$$= \frac{m}{kT} \int_0^\infty v_z^3 \exp\left\{-\frac{mv_z^2}{2kT}\right\} dv_z$$

$$= \frac{m}{kT}\,\frac{kT}{m}\,\frac{2kT}{m} \int_0^\infty y e^{-y}\, dy = \frac{2kT}{m}\,\Gamma(2)$$

Using $\Gamma(2) = 1$, one obtains

$$\langle v_z^2 \rangle^* = \frac{2kT}{m}$$

The mean squared velocities in the x- and y-directions, on the other hand, have the same value as in the interior of the container:

$$\langle v_x^2 \rangle^* = \langle v_y^2 \rangle^* = \langle v_x^2 \rangle = \langle v_y^2 \rangle = \frac{kT}{m}$$

The mean kinetic energy of the particles leaving the container is

$$\langle \epsilon_{kin} \rangle^* = \frac{1}{2} m \left(\langle v_x^2 \rangle^* + \langle v_y^2 \rangle^* + \langle v_z^2 \rangle^* \right) = 2kT$$

It is thus larger than that of the particles in the interior of the container, where it is only $\frac{3}{2}kT$. Equation (7.65) directly yields the rate $R = d^2N/dt\, dA$ by integration over all velocities;

$$R = \frac{d^2N}{dA\, dt} = \frac{N}{V} \int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y \int_{-\infty}^{+\infty} dv_z v_z f(\vec{v}) \qquad \textbf{(7.68)}$$

Note, that here the distribution $f(\vec{v})$ appears in the interior of the container and not $f^*(\vec{v})$. In principle, Equation (7.68) can be directly integrated with Maxwell's velocity distribution. For our calculation, however, we choose a more general way, which remains correct for each distribution $f(\vec{v})$ that depends only on the absolute value $|\vec{v}|$ of velocity. To do this we substitute spherical polar coordinates. We have to take into account that due to $v_z > 0$, θ has to be restricted to the angular interval $\theta \in [0, \pi/2]$:

$$R = \frac{N}{V} \int_0^\infty v^2\, dv \int_0^{\pi/2} \sin\theta\, d\theta \int_0^{2\pi} d\phi v \cos\theta f(v)$$

The two angular integrals can immediately be calculated ($\sin\theta \cos\theta\, d\theta = \sin\theta\, d(\sin\theta)$),

$$R = \frac{N}{V} \pi \int_0^\infty v^3 f(v)\, dv$$

In the preceding exercise we have already introduced the distribution of the absolute values of the velocities, $F(v) = 4\pi v^2 f(v)$, so that

$$R = \frac{1}{4}\,\frac{N}{V} \int_0^\infty v F(v)\, dv = \frac{1}{4}\,\frac{N}{V}\,\langle v \rangle$$

The rate of the evaporating particles increases with the particle density N/V and the mean absolute value of velocity $\langle v \rangle$. For the special case of an ideal gas we obtain with $\langle v \rangle$, according to Equation (7.64),

$$R = \frac{N}{V} \sqrt{\frac{kT}{2\pi m}}$$

To calculate the force acting on the container because of the repulsion of the particles, we first determine the momentum which is carried away by the particles per unit time in z-direction. In the mean, the particles have the momentum $\langle p_z \rangle^* = m \langle v_z \rangle^*$, and for a hole of area A, there are exactly RA particles leaving per unit time. Therefore, the force F_z (on the container) is

$$F_z = -RAm \langle v_z \rangle^* = -\frac{N}{V}\sqrt{\frac{kT}{2\pi m}}\, Am\sqrt{\frac{\pi kT}{2m}}$$
$$= -\frac{1}{2}\frac{N}{V} kTA = -\frac{1}{2} pA$$

Up to the factor $\frac{1}{2}$, which comes about by the fact that the particles are *not* reflected at the hole, F_z is given by the pressure p on the area A. The minus sign corresponds to the negative z-direction, in which the container is accelerated.

Calculation of observables as ensemble averages

In the introduction to ensemble theory we assumed that all observables can be written as the mean value over the ensembles with respect to an appropriate function $f(\vec{r}_i, \vec{p}_i)$:

$$\langle f(\vec{r}_i, \vec{p}_i) \rangle = \frac{1}{h^{3N}} \int d^{3N}r\, d^{3N}p \rho(\vec{r}_i, \vec{p}_i) f(\vec{r}_i, \vec{p}_i) \tag{7.69}$$

Thus the phase-space density $f(\vec{r}_i, \vec{p}_i)$ contains all the information about the system which can be provided by statistical mechanics. Now we want to consider which functions $f(\vec{r}_i, \vec{p}_i)$ have to be chosen to obtain certain observables. As we already know, the entropy is given as the ensemble average of $f_S(\vec{r}_i, \vec{p}_i) = -k \ln \rho(\vec{r}_i, \vec{p}_i)$:

$$S = \langle -k \ln \rho \rangle \tag{7.70}$$

On the other hand, from Equation (7.70) we can determine the thermodynamic potentials $S(E, V, N)$ (microcanonical) and $F(T, V, N)$ (canonical). Therefore Equation (7.70) already contains all thermodynamic properties of the system. These properties therefore need not be calculated by Equation (7.69); for the first step it is sufficient to calculate $S(E, V, N)$ or $F(T, V, N)$ from Equation (7.70). Then all other thermodynamic quantities follow just as in Chapter 4. Of course, one can also write down the functions $f(\vec{r}_i, \vec{p}_i)$ corresponding to a certain quantity. So, for instance, the internal energy is given as the mean value of the Hamiltonian:

$$U = \langle H(\vec{r}_i, \vec{p}_i) \rangle \tag{7.71}$$

However, with the aid of Equation (7.69) one can also obtain observables, which thermodynamics does not tell us anything about. For instance, the phase-space density is such an observable:

$$\rho(\vec{r}_1', \ldots, \vec{r}_N', \vec{p}_1', \ldots, \vec{p}_N') = \left\langle h^{3N} \prod_{i=1}^{N} \delta(\vec{r}_i - \vec{r}_i') \, \delta(\vec{p}_i - \vec{p}_i') \right\rangle \tag{7.72}$$

The delta functions in Equation (7.72) just cancel the integral in Equation (7.69) and yield the integrand at the points $\vec{r}_1', \ldots, \vec{r}_N', \vec{p}_1', \ldots, \vec{p}_N'$. We remark that, strictly speaking, Equation (7.69) stands for a *general mapping of the phase-space density on the real numbers*. Such a mapping is given by the distributions $f(\vec{r}_i, \vec{p}_i)$. In analogy to Equation (7.72), the *phase-space distribution of the particle i* results from $\rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)$ (distinguishable particles):

$$\rho_i(\vec{r}, \vec{p}) = \langle h^3 \delta(\vec{r}_i - \vec{r})\, \delta(\vec{p}_i - \vec{p}) \rangle \tag{7.73}$$

For noninteracting systems $\rho_i(\vec{r}, \vec{p})$ is identical to the corresponding single-particle distribution $\rho(\vec{r}_1, \vec{p}_1)$. For interacting systems this is not true, since Equation (7.73) then also contains the action of the other particles on particle i. In the same way, one obtains the *density of particles i* in coordinate space,

$$\rho_i(\vec{r}) = \langle \delta(\vec{r}_i - \vec{r}) \rangle \tag{7.74}$$

or the *momentum distribution of particle i*,

$$\rho_i(\vec{p}) = \langle \delta(\vec{p}_i - \vec{p}) \rangle \tag{7.75}$$

The *total particle density in coordinate space* is

$$\rho(\vec{r}) = \left\langle \sum_{i=1}^{N} \delta(\vec{r}_i - \vec{r}) \right\rangle \tag{7.76}$$

and the *total momentum distribution* is

$$\rho(\vec{p}) = \left\langle \sum_{i=1}^{N} \delta(\vec{p}_i - \vec{p}) \right\rangle \tag{7.77}$$

Observe the different normalizations of the quantities (7.74–77)

$$\int d^3\vec{r}\, \rho_i(\vec{r}) = \int d^3\vec{p}\, \rho_i(\vec{p}) = 1 \tag{7.78}$$

$$\int d^3\vec{r}\, \rho(\vec{r}) = \int d^3\vec{p}\, \rho(\vec{p}) = N \tag{7.79}$$

Another very interesting quantity is the distribution of the *relative distances of two particles*, or the relative momenta. These follow from

$$f_{ik}(r) = \langle \delta(r - |\vec{r}_i - \vec{r}_k|) \rangle \tag{7.80}$$

The distribution $f_{ik}(r)$ is the probability density for finding the particles i and k at a separation r. The distribution of the absolute relative momenta reads

$$f_{ik}(p) = \langle \delta(p - |\vec{p}_i - \vec{p}_k|) \rangle \tag{7.81}$$

The mean distance of the particles i and k is

$$\langle r_{ik} \rangle = \langle |\vec{r}_i - \vec{r}_k| \rangle = \int_0^\infty r f_{ik}(r)\, dr \tag{7.82}$$

The second equation in (7.82) follows, if Equation (7.80) is inserted for $f_{ik}(r)$ and if the averaging procedure and the integration are exchanged. Analogously, the mean relative momentum of particles i and k is given by

$$\langle p_{ik} \rangle = \langle |\vec{p}_i - \vec{p}_k| \rangle = \int_0^\infty p f_{ik}(p)\, dp \tag{7.83}$$

Correspondingly, one can also calculate the distributions for the relative distances of three particles, or the probability for several particles to come very close to each other (cluster or droplet formation), etc. The practical calculation for such *n-particle correlation functions*, however, can become very complicated in the case of real gases.

Example 7.7: $\rho_i(\vec{r})$ for the ideal gas

Calculate $\rho_i(\vec{r})$ according to Equation (7.74) for an ideal gas.

The phase-space density for the ideal gas is

$$\rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) = N! \prod_{i=1}^{N} \frac{\exp\left\{-\frac{\beta}{2m}\vec{p}_i^{\,2}\right\}}{Z(T, V, 1)} = N! \prod_{i=1}^{N} \rho_i(\vec{r}_i, \vec{p}_i)$$

with the one-particle partition function

$$Z(T, V, 1) = \frac{1}{h^3} \int d^3\vec{r}\, d^3\vec{p} \exp\left\{-\frac{\beta}{2m}\vec{p}^{\,2}\right\} = \frac{V}{\lambda^3}$$

Thus, one has

$$\begin{aligned} \rho_i(\vec{r}) &= \frac{1}{N! h^{3N}} \int d^{3N}\vec{r}\, d^{3N}\vec{p} \\ &\quad \times \rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)\, \delta(\vec{r}_i - \vec{r}) \\ &= \frac{1}{h^{3N}} \int d^{3N}\vec{r}\, d^{3N}\vec{p} \prod_{k=1}^{N} \rho_k(\vec{r}_k, \vec{p}_k)\, \delta(\vec{r}_i - \vec{r}) \end{aligned}$$

Since the one-particle distributions $\rho_k(\vec{r}_k, \vec{p}_k)$ are also normalized to 1, all integrals except that over $\vec{r}_i$, $\vec{p}_i$ yield a factor 1,

$$\begin{aligned} \rho_i(\vec{r}) &= \frac{1}{h^3} \int d^3\vec{r}_i\, d^3\vec{p}_i \frac{\lambda^3}{V} \exp\left\{-\frac{\beta}{2m}\vec{p}_i^{\,2}\right\} \delta(\vec{r}_i - \vec{r}) \\ &= \frac{1}{V} \frac{\lambda^3}{h^3} \int d^3\vec{p}_i \exp\left\{-\frac{\beta}{2m}\vec{p}_i^{\,2}\right\} \end{aligned}$$

The momentum integral together with the factor h^{-3} gives a factor λ^{-3}, which cancels:

$$\rho_i(\vec{r}) = \frac{1}{V}$$

The probability density of finding any of the N particles at the point $\vec{r}$, is constant over the whole container. The total particle density is

$$\rho(\vec{r}) = \left\langle \sum_{i=1}^{N} \delta(\vec{r}_i - \vec{r}) \right\rangle = \sum_{i=1}^{N} \rho_i(\vec{r}) = \frac{N}{V}$$

Exercise 7.8: The law of atmospheres

Consider an air column above the surface of earth with a basis area A. Calculate the density distribution of the particles in the column under the influence of gravitation, at a given temperature T. Assume that the air behaves like an ideal gas and assume gravity to be constant. (See Figure 7.4.)

Solution The Hamiltonian of the system reads

$$H(\vec{r}_i, \vec{p}_i) = \sum_{i=1}^{N} \left(\frac{\vec{p}_i^{\,2}}{2m} + mgz_i \right) = \sum_{i=1}^{N} h_i(\vec{r}_i, \vec{p}_i)$$

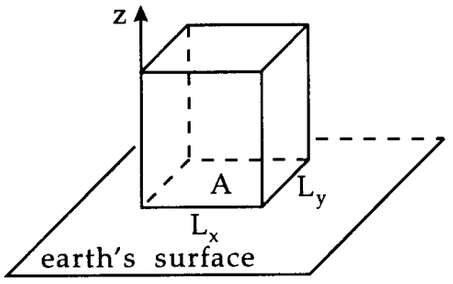


Figure 7.4. The law of atmospheres.

if there are N particles in the air column. Since we are dealing with a system of noninteracting indistinguishable particles, we have

$$\rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) = N! \prod_{i=1}^{N} \frac{\exp\{-\beta h_i(\vec{r}_i, \vec{p}_i)\}}{Z(T, V, 1)}$$

$$= N! \prod_{i=1}^{N} \rho_i(\vec{r}_i, \vec{p}_i)$$

The one-particle partition function can be easily calculated,

$$Z(T, V, 1) = \frac{1}{h^3} \int d^3p \exp\left\{ -\frac{\beta}{2m} \vec{p}^{\,2} \right\} \int d^3r \exp\{-\beta mgz\}$$

The momentum integral, together with h^{-3}, equals λ^{-3}, and the integrals over x and y yield the basis area A of the air column,

$$Z(T, V, 1) = \frac{A}{\lambda^3} \int_0^\infty dz \exp\{-\beta mgz\} = \frac{A}{\beta mg\lambda^3}$$

The definition of the single-particle density is

$$\rho_i(\vec{r}) = \frac{1}{N! h^{3N}} \int d^{3N}\vec{r}\, d^{3N}\vec{p}$$

$$\times \rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)\, \delta(\vec{r}_i - \vec{r})$$

$$= \frac{1}{h^{3N}} \int d^{3N}\vec{r}\, d^{3N}\vec{p} \prod_{k=1}^{N} \rho_k(\vec{r}_k, \vec{p}_k)\, \delta(\vec{r}_i - \vec{r})$$

Due to the normalization of the $\rho_k(\vec{r}_k, \vec{p}_k)$, all integrals except the one over $\vec{r}_i$, $\vec{p}_i$ yield the factor 1,

$$\rho_i(\vec{r}) = \frac{\beta mg\lambda^3}{Ah^3} \int d^3\vec{p}_i \exp\left\{ -\frac{\beta}{2m} \vec{p}_i^{\,2} \right\} \int d^3\vec{r}_i \exp\{-\beta mgz_i\}\, \delta(\vec{r}_i - \vec{r})$$

The momentum integral together with h^{-3} equals λ^{-3} and thus cancels the factor λ^3. The integral over the coordinates cancels because of the δ-function,

$$\rho_i(\vec{r}) = \frac{\beta mg}{A} \exp\{-\beta mgz\}$$

For the N particles in the air column the total density distribution is

$$\rho(\vec{r}) = \frac{N\beta mg}{A} \exp\{-\beta mgz\}$$

It does not depend on x or y, and it decreases exponentially with the height z. If one writes the particle density $\rho(z)$ with the aid of the ideal gas law,

$$\rho(z) = \frac{p(z)}{kT}$$

one obtains for the pressure in the height z:

$$p(z) = \frac{Nmg}{A} \exp\{-\beta mgz\} = p(0) \exp\{-\beta mgz\}$$

The pressure at the surface $p(0) = Nmg/A$ corresponds to the gravitational force of the N particles on the basis area A.

Exercise 7.9: Relative momenta in the ideal gas

Calculate the distribution of the absolute values of the relative momenta of two particles in an ideal gas.

Solution

According to Equation (7.81) we have

$$\begin{aligned} f_{ik}(p) &= \langle \delta(p - |\vec{p}_i - \vec{p}_k|) \rangle \\ &= \frac{1}{N! h^{3N}} \int d^{3N}\vec{r}\, d^{3N}\vec{p}\, \rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)\, \delta(p - |\vec{p}_i - \vec{p}_k|) \\ &= \frac{1}{h^{3N}} \int d^{3N}\vec{r}\, d^{3N}\vec{p} \prod_{l=1}^{N} \rho_l(\vec{r}_l, \vec{p}_l)\, \delta(p - |\vec{p}_i - \vec{p}_k|) \end{aligned}$$

Because of the normalization of the ρ_l, all integrals except those corresponding to the indices i and k yield a factor 1, respectively,

$$\begin{aligned} f_{ik}(p) = \frac{1}{h^6} &\int d^3\vec{p}_i \int d^3\vec{p}_k \int d^3\vec{r}_i \int d^3\vec{r}_k \frac{\lambda^6}{V^2} \\ &\times \exp\left\{-\frac{\beta}{2m}\left(\vec{p}_i^{\,2} + \vec{p}_k^{\,2}\right)\right\} \delta(p - |\vec{p}_i - \vec{p}_k|) \end{aligned}$$

The two integrals over the coordinates cancel the factor V^{-2}. To be able to calculate the momentum integrals, it is convenient to transform to the momentum of the center of mass $\vec{K} = (\vec{p}_i + \vec{p}_k)/2$, and the relative momentum $\vec{p}_{ik} = \vec{p}_i - \vec{p}_k$. Then we have

$$\vec{p}_i = \vec{K} + \frac{1}{2}\vec{p}_{ik} \quad \text{and} \quad \vec{p}_k = \vec{K} - \frac{1}{2}\vec{p}_{ik} \quad \text{as well as} \quad \vec{p}_i^{\,2} + \vec{p}_k^{\,2} = 2\vec{K}^2 + \frac{1}{2}\vec{p}_{ik}^{\,2}$$

and thus

$$f_{ik}(p) = \frac{\lambda^6}{h^6} \int d^3\vec{p}_{ik} \exp\left\{-\frac{\beta}{4m}\vec{p}_{ik}^{\,2}\right\} \delta(p - p_{ik}) \int d^3\vec{K} \exp\left\{-\frac{\beta}{m}\vec{K}^2\right\} \qquad (7.84)$$

(*Remark:* The Jacobi determinant of the coordinate transformation has the absolute value 1.) All integrals over the components of the center-of-mass momentum have the value $\sqrt{m\pi/\beta}$. In

the integral over $\vec{p}_{ik}$ one can introduce polar coordinates, and Equation (7.84) can be rewritten as

$$f_{ik}(p) = \frac{\lambda^6}{h^6}\left(\frac{m\pi}{\beta}\right)^{3/2} 4\pi \int_0^\infty p_{ik}^2 \exp\left\{-\frac{\beta}{4m}p_{ik}^2\right\} \delta(p - p_{ik})\, dp_{ik}$$

$$f_{ik}(p) = \frac{\pi}{2}\left(\frac{1}{\pi mkT}\right)^{3/2} p^2 \exp\left\{-\frac{\beta}{4m}p^2\right\}$$

Because of

$$\begin{aligned}\int_0^\infty f_{ik}(p)\, dp &= \frac{\pi}{2}\left(\frac{1}{\pi mkT}\right)^{3/2} \int_0^\infty p^2 \exp\left\{-\frac{\beta}{4m}p^2\right\} dp \\ &= \frac{\pi}{2}\left(\frac{1}{\pi mkT}\right)^{3/2} \frac{2m}{\beta}\sqrt{\frac{4m}{\beta}} \int_0^\infty y^{1/2} e^{-y}\, dy \\ &= \frac{\pi}{2}\left(\frac{1}{\pi mkT}\right)^{3/2} 4(mkT)^{3/2}\Gamma\left(\frac{3}{2}\right) = 1\end{aligned}$$

this distribution is normalized ($\Gamma(3/2) = \sqrt{\pi}/2$). As one can see, the distribution of the relative momenta is again a Maxwell distribution, however, with different coefficients and a different argument in the exponential function.

Exercise 7.10: Mean distance of two particles

Calculate the probability density of finding two particles of an ideal gas at a distance r, if they are contained in a spherical container of radius K. What is the mean distance of two particles in this sphere?

Solution

Analogous to the preceding exercise we must calculate

$$\begin{aligned}f_{ik}(r) &= \langle \delta(r - |\vec{r}_i - \vec{r}_k|)\rangle \\ &= \frac{1}{N!h^{3N}} \int d^{3N}\vec{r}\, d^{3N}\vec{p} \\ &\quad \times \rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)\, \delta(r - |\vec{r}_i - \vec{r}_k|) \\ &= \frac{1}{h^{3N}} \int d^{3N}\vec{r}\, d^{3N}\vec{p} \prod_{l=1}^{N} \rho_l(\vec{r}_l, \vec{p}_l)\, \delta(r - |\vec{r}_i - \vec{r}_k|)\end{aligned}$$

Because of the normalization of the ρ_l, all integrals except those corresponding to the indices i and k yield a factor 1, respectively,

$$\begin{aligned}f_{ik}(r) &= \frac{1}{h^6} \int d^3\vec{p}_i \int d^3\vec{p}_k \int d^3\vec{r}_i \int d^3\vec{r}_k \frac{\lambda^6}{V^2} \\ &\quad \times \exp\left\{-\frac{\beta}{2m}\left(\vec{p}_i^{\,2} + \vec{p}_k^{\,2}\right)\right\} \delta(r - |\vec{r}_i - \vec{r}_k|)\end{aligned}$$

The momentum integrals together with the factor h^{-6} yield λ^{-6}, which cancels the factor λ^6,

$$f_{ik}(r) = \frac{1}{V^2} \int d^3\vec{r}_i \int d^3\vec{r}_k\, \delta(r - |\vec{r}_i - \vec{r}_k|) \qquad \textbf{(7.85)}$$

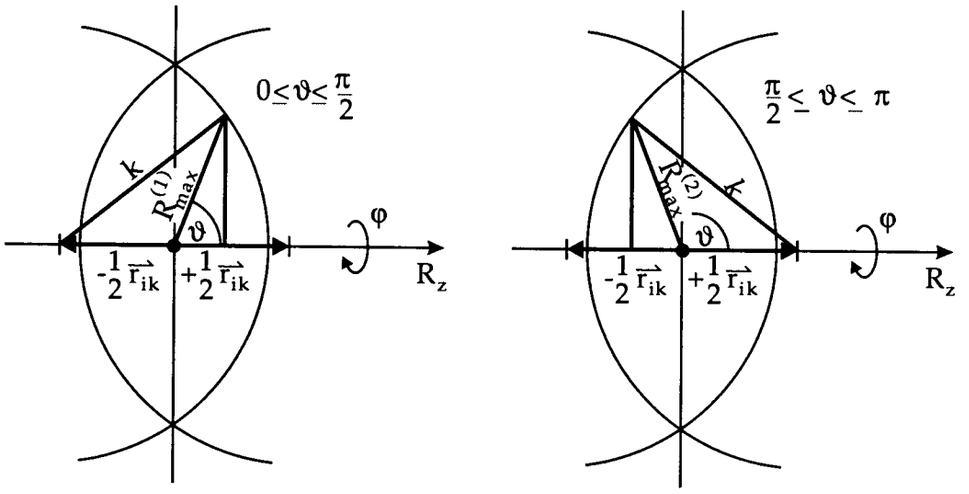


Figure 7.5. Concerning the geometry of the R– and r_{ik}–integrations.

To evaluate the remaining integrals, one substitutes center-of-mass and relative coordinates:

$$\vec{R} = \frac{1}{2}(\vec{r}_i + \vec{r}_k), \qquad \vec{r}_{ik} = \vec{r}_i - \vec{r}_k \tag{7.86}$$

$$\vec{r}_i = \vec{R} + \frac{1}{2}\vec{r}_{ik}, \qquad \vec{r}_k = \vec{R} - \frac{1}{2}\vec{r}_{ik} \tag{7.87}$$

Since the integrations in Equation (7.85) extend only over the finite spherical volume, the integration limits must also be recalculated for the new variables. In Equation (7.85) the vectors $\vec{r}_i$ and $\vec{r}_k$ must fulfill the conditions

$$\vec{r}_i^{\,2} \leq \vec{K}^2 \qquad \text{and} \qquad \vec{r}_k^{\,2} \leq \vec{K}^2$$

In the new coordinates these conditions read

$$\left(\vec{R} + \frac{1}{2}\vec{r}_{ik}\right)^2 \leq K^2 \qquad \text{and} \qquad \left(\vec{R} - \frac{1}{2}\vec{r}_{ik}\right)^2 \leq K^2 \tag{7.88}$$

Equation (7.85) transforms into

$$f_{ik}(r) = \frac{1}{V^2}\int d^3\vec{r}_{ik} \int d^3\vec{R}\,\delta(r - r_{ik})$$

where we have to integrate over all vectors $\vec{r}_{ik}$ and $\vec{R}$, which fulfill the constraints (7.88) (as we have seen in the preceding exercise, the absolute value of the Jacobi determinant of the transformation (7.86–87) is just equal to 1).

If the integral over $\vec{r}_{ik}$ is interpreted as the exterior integral, the vector $\vec{r}_{ik}$ is fixed with respect to the inner integration over $\vec{R}$. We must have $|r_{ik}| \leq 2K$, because the relative distance of the particles i and k cannot exceed twice the sphere radius.

If the vector $\vec{r}_{ik}$ is given, conditions (7.88) can be interpreted geometrically. All vectors $\vec{R}$ in the interior of a sphere of radius K with its origin at $-(1/2)\vec{r}_{ik}$ fulfill the first condition, and all vectors $\vec{R}$ in the interior of a sphere of radius K with the origin $+(1/2)\vec{r}_{ik}$ fulfill the second condition. Thus for a given $\vec{r}_{ik}$, all vectors $\vec{R}$ in the interior of the overlap region of the two spheres (Figure 7.5) fulfill conditions (7.88). Since one is still free to choose the coordinate system for the $\vec{R}$-integration, it is most convenient to place the R_z-axis along the direction of the vector $\vec{r}_{ik}$.

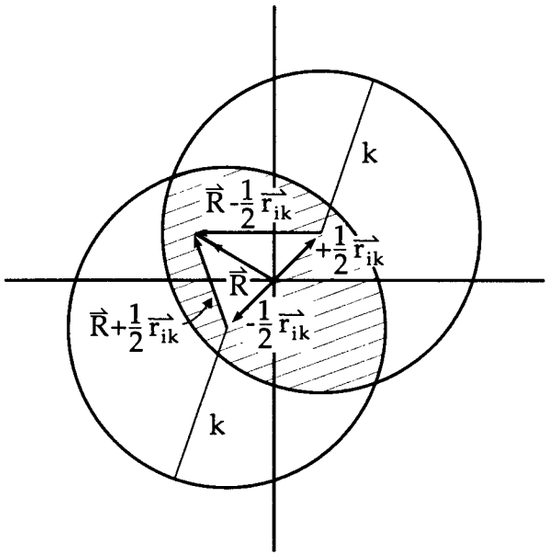


Figure 7.6. Conditions (7.88).

If one finally passes over to polar coordinates, the integration limits for the $\vec{R}$-integration follow from Figures 7.5 and 7.6. For $0 \leq \theta \leq \pi/2$, $|\vec{R}|$ can assume all values between $0 \leq |\vec{R}| \leq R^{(1)}_{\max}(\theta, r_{ik})$, where $R^{(1)}_{\max}(\theta, r_{ik})$ must be determined by the condition

$$\left(\frac{1}{2} r_{ik} + R^{(1)}_{\max} \cos\theta\right)^2 + \left(R^{(1)}_{\max} \sin\theta\right)^2 = K^2 \tag{7.89}$$

Analogously, for $\pi/2 \leq \theta \leq \pi$, $|\vec{R}|$ can assume all values between $0 \leq |\vec{R}| \leq R^{(2)}_{\max}(\theta, r_{ik})$, where $R^{(2)}_{\max}(\theta, r_{ik})$ now must fulfill the condition

$$\left(\frac{1}{2} r_{ik} - R^{(2)}_{\max} \cos\theta\right)^2 + \left(R^{(2)}_{\max} \sin\theta\right)^2 = K^2 \tag{7.90}$$

First one determines $R^{(1)}_{\max}$ and $R^{(2)}_{\max}$ by solving the quadratic Equations (7.89) and (7.90):

$$R^{(1)}_{\max} = \frac{1}{2}\left\{-r_{ik}\cos\theta \pm \left[r_{ik}^2 \cos^2\theta - \left(r_{ik}^2 - 4K^2\right)\right]^{1/2}\right\} \qquad \text{for} \quad 0 \leq \theta \leq \frac{\pi}{2} \tag{7.91}$$

$$R^{(2)}_{\max} = \frac{1}{2}\left\{r_{ik}\cos\theta \pm \left[r_{ik}^2 \cos^2\theta - \left(r_{ik}^2 - 4K^2\right)\right]^{1/2}\right\} \qquad \text{for} \quad \frac{\pi}{2} \leq \theta \leq \pi \tag{7.92}$$

In both cases, the solution with the positive sign has to be chosen: In Equation (7.91) $\cos\theta \geq 0$, and to obtain $R^{(1)}_{\max} \geq 0$, the positive sign has to be chosen. Correspondingly, in Equation (7.92) $\cos\theta \leq 0$, and again the positive sign must be chosen. Using the abbreviations $x = \cos\theta$ and $c^2 = (4K^2/r_{ik}^2 - 1)$, Equations (7.91) and (7.92) can be rewritten as

$$R^{(1)}_{\max} = \frac{r_{ik}}{2}\left\{\left(x^2 + c^2\right)^{1/2} - x\right\}$$

$$R^{(2)}_{\max} = \frac{r_{ik}}{2}\left\{\left(x^2 + c^2\right)^{1/2} + x\right\}$$

Now the integral reads

$$f_{ik}(r) = \frac{1}{V^2} \int_{|\vec{r}_{ik}|^2 \le 4K^2} d^3\vec{r}_{ik}\, \delta(r - r_{ik}) \int_0^{2\pi} d\phi \left[\int_0^{\pi/2} \sin\theta\, d\theta \int_0^{R^{(1)}_{\max}} R^2\, dR \right.$$
$$\left. + \int_{\pi/2}^{\pi} \sin\theta\, d\theta \int_0^{R^{(2)}_{\max}} R^2\, dR \right]$$

The ϕ-integration simply yields the factor 2π. Performing also the R-integrations and substituting $x = \cos\theta$, one is left with

$$f_{ik}(r) = \frac{1}{V^2} \frac{2\pi}{3} \int_{r_{ik}^2 \le 4K^2} d^3\vec{r}_{ik}\, \delta(r - r_{ik})$$
$$\times \left[\int_0^1 dx \left(R^{(1)}_{\max}(x, r_{ik})\right)^3 + \int_{-1}^0 dx \left(R^{(2)}_{\max}(x, r_{ik})\right)^3 \right] \tag{7.93}$$

In the next step we turn to the x-integrals,

$$I(r_{ik}) = \left(\frac{r_{ik}}{2}\right)^3 \left[\int_0^1 dx \left\{ \left(x^2 + c^2\right)^{1/2} - x \right\}^3 + \int_{-1}^0 dx \left\{ \left(x^2 + c^2\right)^{1/2} + x \right\}^3 \right]$$

If we substitute $x \to -x$ in the second integral, we can see that the latter must have the same value as the first:

$$I(r_{ik}) = \frac{r_{ik}^3}{4} \int_0^1 dx \left\{ \left(x^2 + c^2\right)^{1/2} - x \right\}^3$$
$$= \frac{r_{ik}^3}{4} \int_0^1 dx \left\{ \left(x^2 + c^2\right)^{3/2} - 3x\left(x^2 + c^2\right) + 3x^2\left(x^2 + c^2\right)^{1/2} - x^3 \right\}$$
$$= \frac{r_{ik}^3}{4} \left\{ \int_0^1 dx \left(x^2 + c^2\right)^{1/2} \left(4x^2 + c^2\right) - \int_0^1 dx \left(4x^3 + 3xc^2\right) \right\}$$

The second integral is elementary, and the first one is simple, if one considers

$$\frac{d}{dx} \left\{ \left(x^2 + c^2\right)^{3/2} x \right\} = \left(x^2 + c^2\right)^{1/2} \left(4x^2 + c^2\right)$$

One obtains

$$I(r_{ik}) = \frac{r_{ik}^3}{4} \left\{ \left(x^2 + c^2\right)^{3/2} x - x^4 - \frac{3}{2} x^2 c^2 \right\}_0^1$$
$$= \frac{r_{ik}^3}{4} \left\{ \left(1 + c^2\right)^{3/2} - 1 - \frac{3}{2} c^2 \right\}$$

Inserting again $c^2 = (4K^2/r_{ik}^2 - 1)$, one obtains

$$I(r_{ik}) = \frac{r_{ik}^3}{4} \left\{ \left(\frac{2K}{r_{ik}}\right)^3 - \frac{3}{2} \left(\frac{2K}{r_{ik}}\right)^2 + \frac{1}{2} \right\}$$

Thus Equation (7.93) can be rewritten

$$f_{ik}(r) = \frac{1}{V^2} \frac{\pi}{6} \int_{r_{ik}^2 \le 4K^2} d^3\vec{r}_{ik}\, \delta(r - r_{ik}) r_{ik}^3 \left\{ \left(\frac{2K}{r_{ik}}\right)^3 - \frac{3}{2} \left(\frac{2K}{r_{ik}}\right)^2 + \frac{1}{2} \right\}$$

The remaining integrals can be solved by substitution of polar coordinates . The angular integration simply yields a factor 4π,

$$f_{ik}(r) = \frac{1}{V^2}\frac{2\pi^2}{3}\int_0^{2K} dr_{ik}\,\delta(r - r_{ik})r_{ik}^5\left\{\left(\frac{2K}{r_{ik}}\right)^3 - \frac{3}{2}\left(\frac{2K}{r_{ik}}\right)^2 + \frac{1}{2}\right\}$$

$$f_{ik}(r) = \frac{1}{V^2}\frac{2\pi^2}{3}r^5\left\{\left(\frac{2K}{r}\right)^3 - \frac{3}{2}\left(\frac{2K}{r}\right)^2 + \frac{1}{2}\right\} \tag{7.94}$$

If one considers $V = 4\pi K^3/3$, one can conveniently rewrite Equation (7.94) as (Figure 7.7):

$$f_{ik}(r) = \frac{12}{K}\left\{\left(\frac{r}{2K}\right)^2 - \frac{3}{2}\left(\frac{r}{2K}\right)^3 + \frac{1}{2}\left(\frac{r}{2K}\right)^5\right\} \tag{7.95}$$

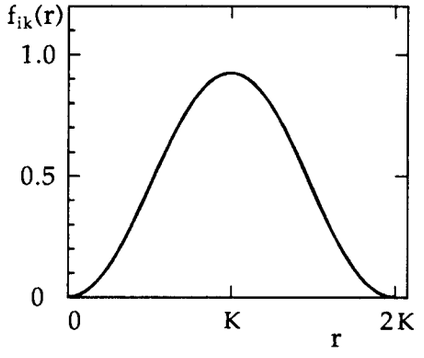


Figure 7.7. The function $f_{ik}(r)$.

The distribution (7.95) is a function of the dimensionless variable $y = r/(2K)$, where $r \in [0, 2K]$. It has a maximum in the vicinity of $r \approx K$ and it vanishes for $r = 0$ and $r = 2K$. This means that both very small distances $r \to 0$ and the maximum distance $r \to 2K$ occur only very scarcely. Most frequently, the distances are comparable to the sphere radius K. Observe that the function $f_{ik}(r)$ is automatically normalized to 1:

$$\int_0^{2K} f_{ik}(r)\,dr = 24\int_0^1 dy\left\{y^2 - \frac{3}{2}y^3 + \frac{1}{2}y^5\right\}$$

$$= 24\left\{\frac{1}{3} - \frac{3}{8} + \frac{1}{12}\right\} = 1$$

The mean distance of the two particles is

$$\langle r_{ik}\rangle = \int_0^{2K} r f_{ik}(r)\,dr = 48K\int_0^1 dy\left\{y^3 - \frac{3}{2}y^4 + \frac{1}{2}y^6\right\}$$

$$= 48K\left\{\frac{1}{4} - \frac{3}{10} + \frac{1}{14}\right\}$$

$$= \frac{36}{35}K$$

It is thus a little larger than the sphere radius K.

Connection between microcanonical and canonical ensembles

The three preceding examples have shown that the canonical ensemble gives essentially the same result as the microcanonical ensemble, although the possible microstates are very different in both cases. Now we want to examine the reason for this coincidence in greater detail.

The probability of finding a system of the canonical ensemble in the microstate (q_ν, p_ν), is (without the Gibbs' factor):

$$dp = \frac{1}{h^{3N}} \rho(q_\nu, p_\nu) d^{3N}q\, d^{3N}p = \frac{1}{h^{3N}Z} \exp\{-\beta H(q_\nu, p_\nu)\}\, d^{3N}q\, d^{3N}p \tag{7.96}$$

This probability is constant on the energy surface $H(q_\nu, p_\nu) = E$ (basic postulate of statistical mechanics). Therefore we can easily calculate the probability of finding a system in any microstate with an energy between E and $E + \Delta E$. To do so, we only have to integrate Equation (7.96) over this energy shell; the integrand is constant in this case:

$$dp(E) = \frac{1}{Z} \exp\{-\beta E\} \frac{1}{h^{3N}} \int_{E \le H(q_\nu, p_\nu) \le E+dE} d^{3N}q\, d^{3N}p \tag{7.97}$$

The last integral has already been calculated many times. It is just the number of all microstates in the energy shell of thickness dE. With the number Σ of states carrying an energy $H(q_\nu, p_\nu) \le E$,

$$\Sigma(E, V, N) = \frac{1}{h^{3N}} \int_{H(q_\nu, p_\nu) \le E} d^{3N}q\, d^{3N}p \tag{7.98}$$

the integral in Equation (7.97) assumes the value

$$\frac{1}{h^{3N}} \int_{E \le H(q_\nu, p_\nu) \le E+dE} d^{3N}q\, d^{3N}p = \frac{\partial \Sigma}{\partial E} dE = g(E) dE \tag{7.99}$$

if $g(E)$ is the density of states, which we have frequently used before. The probability of finding a system in a thin energy shell between E and $E + dE$, is therefore given by

$$dp(E) = p(E)\, dE = \frac{1}{Z} g(E) \exp\{-\beta E\}\, dE \tag{7.100}$$

Of course, the partition function Z can also be expressed with the aid of $g(E)$:

$$\begin{aligned} Z(T, V, N) &= \frac{1}{h^{3N}} \int d^{3N}q\, d^{3N}p \exp\{-\beta H(q_\nu, p_\nu)\} \\ &= \int dE g(E) \exp\{-\beta E\} \end{aligned} \tag{7.101}$$

In the case of discrete quantum mechanical states, the density of states $g(E)$ is replaced by the *degeneration factor* g_E, which denotes *the number of quantum mechanical states which have exactly the same energy.* Since in quantum mechanics the stationary states with energy E can be calculated, Equations (7.100) and (7.101) can be directly transformed to quantum mechanics. Then

$$p(E) = \frac{g_E}{Z} \exp\{-\beta E\} \tag{7.102}$$

is the probability for the quantum mechanical system to assume one of the g_E energy states E. However, this does not yet have anything to do with quantum statistics, since in this case we are also dealing with distinguishable particles. The theory which has been presented up to now is called *Maxwell-Boltzmann statistics.* This theory starts from enumerable

particles and is afterwards corrected with the Gibbs factor, if "in real life" the particles are indistinguishable. In true quantum statistics this will be no longer necessary.

Equation (7.101) now provides a very interesting relation between the canonical and microcanonical ensembles. On the one hand, we have calculated the density of states $g(E)$, which is tightly connected to Ω, and on the other hand, the integration in (7.101) yields the canonical partition function (free energy). Even the converse of this statement is true. If $Z(\beta, V, N)$ is known, one can use this to calculate $g(E)$. To do this, in Equation (7.101) $\beta = 1/kT$ is interpreted as a formal parameter, which may also be complex. Now we consider the analytic continuation of $Z(\beta)$ (V and N = const.) to the complex β-plane. Then

$$Z(\beta) = \int_0^\infty dE g(E) e^{-\beta E} \tag{7.103}$$

is an analytic function of β, if $\Re\beta > 0$. The relation $\Re\beta > 0$ guarantees that the integrand in Equation (7.103) is bounded for all energies and that the integral exists. Equation (7.103) is just the definition of a Laplace transformation of the function $g(E)$. In some sense here, the Laplace transformation is an extension of the Fourier transformation. If β were purely imaginary, then Equation (7.103) would be exactly a Fourier transformation, which also has a reverse transformation.

For the Laplace transformation one can also write down a reverse transformation. To find it, we multiply Equation (7.103) by $e^{\beta E'}$ and integrate over the integration path C in the complex plane, with $\beta = \beta' + i\beta''$ (β', β'' real) and $\beta' > 0$ (arbitrary), which is depicted in Figure 7.8,

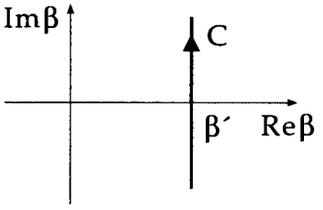


Figure 7.8. Integration path for Equation (7.104).

$$\int_{\beta'-i\infty}^{\beta'+i\infty} d\beta\, Z(\beta) e^{\beta E'} = \int_{\beta'-i\infty}^{\beta'+i\infty} d\beta \int_0^\infty e^{\beta(E'-E)} g(E)\, dE \tag{7.104}$$

Since the integrand is analytic due to $\Re\beta > 0$, on the righthand side of Equation (7.104) the order of integrations may be exchanged. Here again the integrand is bounded and analytical for large E and $\Re\beta > 0$. With $d\beta = d\beta' + id\beta'' = id\beta''$ for arbitrary but fixed $\beta' > 0$ we obtain

$$\int_{\beta'-i\infty}^{\beta'+i\infty} d\beta\, e^{\beta(E'-E)} = i \int_{-\infty}^{+\infty} d\beta'' e^{(\beta'+i\beta'')(E'-E)} = e^{\beta'(E'-E)} 2\pi i\, \delta(E' - E) \tag{7.105}$$

where we have used the well-known formula $\int_{-\infty}^{\infty} dx e^{ikx} = 2\pi\delta(k)$. Inserting this into Equation (7.104) yields

$$\int_{\beta'-i\infty}^{\beta'+i\infty} d\beta\, Z(\beta) e^{\beta E'} = \int_0^\infty dE e^{\beta'(E'-E)} 2\pi i\, \delta(E' - E) g(E)$$

$$= 2\pi i g(E') \tag{7.106}$$

Hence we have found the inverse of the Laplace transformation

$$g(E) = \frac{1}{2\pi i} \int_{\beta'-i\infty}^{\beta'+i\infty} d\beta \, e^{\beta E} Z(\beta) \tag{7.107}$$

The real part $\Re\beta = \beta'$ in this case is arbitrary but it must hold that $\beta' > 0$ (so that Equation (7.103) remains analytical).

Example 7.11: The ideal gas

We want to check Equations (7.103) and (7.107) explicitly for an ideal gas. First we calculate $g(E)$, using $\Sigma(E)$ from Equation (5.56), which including the Gibbs factor $1/N!$ reads

$$\Sigma(E, V, N) = \frac{V^N}{h^{3N} N!} \frac{\pi^{3N/2}}{\frac{3N}{2}\Gamma(\frac{3N}{2})} (2mE)^{3N/2}$$

and thus

$$g(E) = \frac{\partial \Sigma}{\partial E} = \frac{V^N}{h^{3N} N!} \frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2})} (2m)^{3N/2} E^{3N/2-1} \tag{7.108}$$

Insertion into Equation (7.103) yields

$$Z(\beta) = \frac{V^N}{h^{3N} N!} \frac{(2m\pi)^{3N/2}}{\Gamma(\frac{3N}{2})} \int_0^\infty dE E^{3N/2-1} e^{-\beta E} \tag{7.109}$$

With the substitution $x = \beta E$ the integral in Equation (7.109) can be reduced to the Γ-function:

$$Z(\beta) = \frac{V^N}{h^{3N} N!} \frac{(2m\pi)^{3N/2}}{\Gamma(\frac{3N}{2})} \left(\frac{1}{\beta}\right)^{3N/2} \int_0^\infty dx x^{3N/2-1} e^{-x}$$

The value of the integral is just $\Gamma(3N/2)$, and we have

$$Z(\beta) = \frac{V^N}{N!} \left(\frac{2m\pi}{h^2\beta}\right)^{3N/2} = \frac{1}{N!} \frac{V^N}{\lambda^{3N}} \qquad \lambda = \left(\frac{h^2}{2\pi mkT}\right)^{\frac{1}{2}} \tag{7.110}$$

as we had already calculated in Example 7.1. Now we want to calculate the density of states $g(E)$ from the partition function (7.110) by using the reverse transformation in Equation (7.107). We have

$$g(E) = \frac{V^N}{N!} \left(\frac{2m\pi}{h^2}\right)^{3N/2} \frac{1}{2\pi i} \int_{\beta'-i\infty}^{\beta'+i\infty} d\beta \, \frac{e^{\beta E}}{\beta^{3N/2}} \tag{7.111}$$

This integral is conveniently evaluated with the aid of the residue theorem. To do this, however, the integration path must be closed, without changing the value of the integral (Figure 7.9). Let us first take $E \geq 0$; then the path (1), extending leftward from $\Im\beta = +\infty$ on a sphere with a radius r ($r \to \infty$) to $\Im\beta = -\infty$, does not contribute. Namely, using $k = 3N/2$ we have

$$\beta = re^{i\phi} \qquad \text{and} \qquad r \to \infty,\ \phi \in \left[\frac{\pi}{2}, \frac{3\pi}{2}\right]$$

$$\frac{e^{\beta E}}{\beta^k} = \frac{\exp\{Er\cos\phi\}\exp\{iEr\sin\phi\}}{r^k e^{ik\phi}} \to 0 \qquad \text{for} \quad r \to \infty \tag{7.112}$$

because $\cos\phi \leq 0$ and because $\exp\{iEr\sin\phi\}$ is bounded for all r. One could argue that on this part of the sphere $\Re\beta < 0$, and thus the condition for the analyticity of Equation (7.103) is not met. Regarding Equation (7.111), one can see that this is not true: The integrand is analytical except for the origin; thus mathematically our argumentation is completely correct.

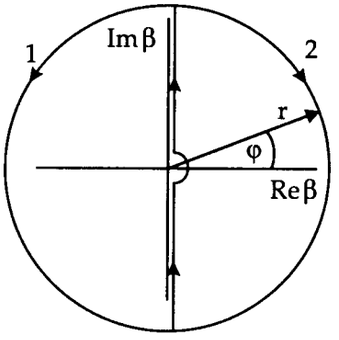


Figure 7.9. Integration path for Equation (7.111).

Analogously, for $E < 0$ path (2) can be used. Then in Equation (7.112) $\cos\phi \geq 0$, but $E < 0$, so that the first exponential factor again vanishes for $r \to \infty$. For $E = 0$ there are no problems either, since in that case the factor r^{-k} vanishes sufficiently fast for $k > 1$.

Because of the residue theorem we can deform the integration path arbitrarily, as long as the path does not leave the region of regularity of the integrand, and as long as all singularities of the integrand remain in the interior of our path.

The integration path parallel to the $\Im\beta$-axis can thus be placed onto this axis (i.e., $\beta' = 0$), only if the pole of the integrand at $\beta = 0$ is passed on the right. Therefore the integral (7.111) for $E < 0$, i.e., on path (2), yields the value zero, since here the integrand is everywhere regular and there are no poles included. On path (1) one single residue at $\beta = 0$ remains to be calculated. To obtain this, we expand the integrand $e^{\beta E}/\beta^k$ into a Laurent series,

$$\frac{e^{\beta E}}{\beta^k} = \sum_{n=0}^{\infty} \frac{E^n}{n!}\beta^{n-k} = \sum_{n=-k}^{\infty} \frac{E^{n+k}}{(n+k)!}\beta^n$$

The residue is the coefficient a_{-1} in front of β^{-1} in the Laurent series, $E^{k-1}/(k-1)!$, so that we finally get

$$\frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} d\beta\, \frac{e^{\beta E}}{\beta^k} = \begin{cases} 0 & E < 0 \\ \dfrac{E^{k-1}}{(k-1)!} & E \geq 0 \end{cases} \tag{7.113}$$

Inserting this into Equation (7.111), and using $k = 3N/2$, we obtain

$$g(E) = \frac{V^N}{N!}\left(\frac{2\pi m}{h^2}\right)^{3N/2} \frac{E^{3N/2-1}}{\Gamma\left(\frac{3N}{2}\right)} \qquad \text{for} \quad E \geq 0 \tag{7.114}$$

which, because of $\Gamma(3N/2) = (3N/2-1)!$, is identical to Equation (7.108). Our derivation of equation (7.113) is valid only for integer k but the result holds as well for noninteger k of $(k-1)!$ is replaced by $\Gamma(k)$. This can be shown by the defintion of the complex Γ-function.

The canonical and the microcanonical ensembles therefore do not only occasionally yield identical results, they contain the same information. Just as the Legendre transformation leads from a closed system with the natural variables (E, V, N) and the thermodynamic potential $S(E, V, N)$ to a system with the given temperature (T, V, N) and a new potential $F(T, V, N)$, the Laplace transformation provides a connection between $\Omega(E, V, N)$ (strictly speaking, $g(E, V, N)$) and $Z(T, V, N)$.

Exercise 7.12: Density of states for N harmonic oscillators

Calculate the density of states $g(E)$ for a system of N harmonic oscillators from the partition function, according to Exercise 7.3.

Solution We have

$$Z(T, V, N) = \left(\frac{kT}{\hbar\omega}\right)^N = (\beta\hbar\omega)^{-N}$$

Using Equation (7.107), this yields the density of states $g(E)$,

$$g(E) = \left(\frac{1}{\hbar\omega}\right)^N \frac{1}{2\pi i} \int_{\beta'-i\infty}^{\beta'+i\infty} d\beta \, \frac{e^{\beta E}}{\beta^N}$$

The integral to be calculated is essentially the same as that of an ideal gas. According to Equation (7.113), we have

$$g(E) = \left(\frac{1}{\hbar\omega}\right)^N \frac{E^{N-1}}{(N-1)!} \qquad \text{for} \quad E \geq 0$$

which exactly coincides with Equation (6.61).

Fluctuations

We want to elucidate the connection between the microcanonical and canonical ensembles once again, from another point of view. To do this we start with Equation (7.100):

$$p_c(E) = \frac{1}{Z} g(E) \exp\{-\beta E\} \tag{7.115}$$

where $p_c(E)$ is the probability density of finding a system at a given temperature ($\beta = 1/(kT)$) at the energy E. At first, we look qualitatively at Equation (7.115).

The density of states $g(E)$, which we have already calculated in several examples, is in general a function which strongly increases with E ($g(E) \propto E^N$, $N \to \infty$). By contrast, the Boltzmann factor $e^{-\beta E}$ decreases exponentially with energy.

Therefore $p_c(E)$ must be a function with a maximum. The maximum, at E^*, corresponds to the most probable energy. It is determined by

$$\frac{\partial p_c(E)}{\partial E} = \frac{1}{Z}\left(\frac{\partial g}{\partial E} - g\beta\right) \exp\{-\beta E\} = 0 \tag{7.116}$$

or

$$\frac{1}{g}\left.\frac{\partial g}{\partial E}\right|_{E=E^*} = \frac{1}{kT} \tag{7.117}$$

Now we know that the number Ω of states in a constant small energy interval ΔE obeys the relation $\Omega = g\,\Delta E$, so that for Equation (7.117) we can also write

$$\left.\frac{\partial \ln \Omega}{\partial E}\right|_{E^*} = \frac{1}{kT} \quad \text{or} \quad \left.\frac{\partial S}{\partial E}\right|_{E^*} = \frac{1}{T} \tag{7.118}$$

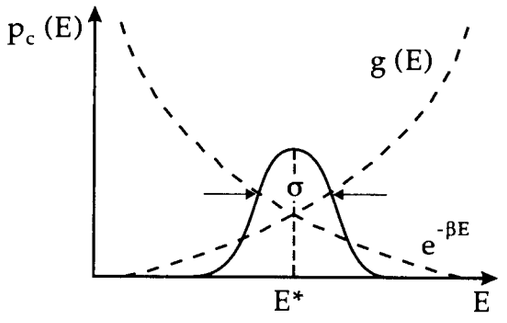


Figure 7.10. $p_c(E)$.

where in Equation (7.117) on the left side we have multipied both numerator and denominator by ΔE, and where we have used $\frac{\partial \Delta E}{\partial E} = 0$. Namely, the thickness ΔE of the energy shell is independent of the energy E. The most probable energy E^* of the canonical ensemble is thus identical to the fixed energy $E_0 = \text{const.}$ of the microcanonical ensemble. Equation (7.118) is just the prescription according to which the temperature in the microcanonical ensemble has to be calculated at a given energy, cf. Equations (4.8) and (4.9). Now the maximum of the function $p_k(E)$ at E^* is simultaneously the mean value $\langle E\rangle$ of all possible energies. This can be seen in the following way: We have

$$\begin{aligned}\langle E\rangle = U &= \frac{1}{Z}\int_0^\infty dE g(E) E \exp\{-\beta E\} \\ &= -\frac{1}{Z}\frac{\partial}{\partial \beta} Z = -\frac{\partial}{\partial \beta}\ln Z(\beta)\end{aligned} \tag{7.119}$$

which because of $F = -kT \ln Z$ and $\beta = 1/(kT)$ can also be rewritten as follows:

$$\begin{aligned}\langle E\rangle = U &= +\frac{\partial}{\partial \beta}\left(\frac{F}{kT}\right) = -kT^2\frac{\partial}{\partial T}\left(\frac{F}{kT}\right) \\ &= F - T\frac{\partial F}{\partial T}\end{aligned} \tag{7.120}$$

Using $\partial F/\partial T|_{V,N} = -S$ (cf. Equation (4.32)), this implies

$$\langle E\rangle = U = F + TS \tag{7.121}$$

i.e., the mean value $\langle E\rangle$ is also identical to the fixed energy E_0 of the microcanonical ensemble, since Equation (7.121) is only the reverse transformation from $F(T, V, N)$ to $U(S, V, N)$, where in the microcanonical case U coincides with the given energy E_0. We have thus derived the general statement:

In the canonical ensemble the most probable energy E^* is identical to the mean value of all energies $\langle E\rangle$ and corresponds to the fixed given energy E_0 of the microcanonical ensemble. The distribution $p_c(E)$ has a sharp maximum at this value, as has been shown in Figure 7.10. In the canonical case all energies E occur at a given temperature, but the

probability decreases very rapidly, if E differs from the value $E^* = \langle E \rangle = U = E_0$. The measure for the width of the canonical distribution is the *standard deviation* σ *from the mean value* $\langle E \rangle$. It is defined by

$$\sigma^2 = \langle E^2 \rangle - \langle E \rangle^2 \tag{7.122}$$

To calculate σ^2, we differentiate Equation (7.119) with respect to β,

$$\frac{\partial U}{\partial \beta} = -\frac{1}{Z} \int_0^\infty dE g(E) E^2 \exp\{-\beta E\} + \frac{1}{Z^2} \left(\int_0^\infty dE g(E) E \exp\{-\beta E\} \right)^2$$

$$= -\left(\langle E^2 \rangle - \langle E \rangle^2 \right) \tag{7.123}$$

With $\beta = 1/kT$ we obtain from Equations (7.122) and (7.123) for the standard deviation

$$\sigma^2 = -\frac{\partial U}{\partial \beta} = kT^2 \left. \frac{\partial U}{\partial T} \right|_{V,N} = kT^2 C_V \tag{7.124}$$

The relative width is the ratio of σ to the mean energy $U = \langle E \rangle$:

$$\frac{\sigma}{\langle E \rangle} = \frac{\sqrt{\sigma^2}}{\langle E \rangle} = \frac{1}{U} \sqrt{kT^2 C_V} \tag{7.125}$$

The total heat capacity, however, is proportional to the particle number N, as is the internal energy U. The relative width of the canonical energy distribution is therefore proportional to $1/\sqrt{N}$ and approaches zero like $\sqrt{N}^{-1}$ for large particle numbers ($N \to \infty$):

$$\frac{\sigma}{\langle E \rangle} = \mathrm{O}\left(\frac{1}{\sqrt{N}} \right) \tag{7.126}$$

With increasing N the maximum becomes ever more strongly peaked. Hence, deviations (fluctuations) from the mean energy $\langle E \rangle$ become less and less probable with increasing N.

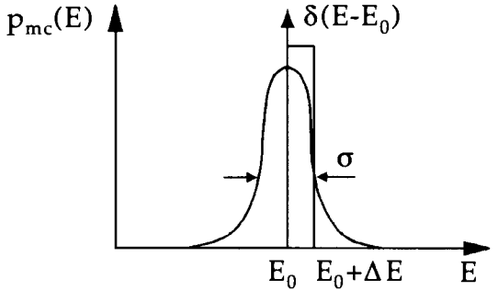


Figure 7.11. $p_{mc}(E)$.

For $N \to \infty$, essentially only the mean energy occurs in the canonical ensemble. In the microcanonical ensemble the energy distribution $p_{mc}(E)$ is simply

$$p_{mc}(E) = \delta(E - E_0) \tag{7.127}$$

if E_0 is the given energy. The canonical distribution for $N \to \infty$ approaches the δ-function more and more.

Recall that for practical calculation the δ-function is very often being replaced by a thin rectangle of width ΔE and the constant area 1. For $N \to \infty$ this has no consequences on the results. For this reason, the canonical and the microcanonical results must coincide for large particle numbers.

One can even express the shape of $p_c(E)$ in the vicinity of the mean energy by purely thermodynamic quantities. To do this, we expand $\ln\{g(E)e^{-\beta E}\}$, in the vicinity of the

maximum E^*, with respect to small deviations from E^*:

$$\ln\{ge^{-\beta E}\} \approx \ln\{ge^{-\beta E}\}|_{E^*} + \frac{1}{2}\frac{\partial^2}{\partial E^2}\ln\{ge^{-\beta E}\}|_{E=E^*}(E-E^*)^2 + \cdots \tag{7.128}$$

Of course, the first derivative vanishes at the maximum. Now $\ln\{ge^{-\beta E}\}|_{E^*} \approx -\beta(U-TS)$ with $\ln g|_{E^*} \approx \ln(g\,\Delta E)|_{E^*} \approx \ln \Omega|_{E^*} = S/k|_{E^*}$; hence the second derivative is given by

$$\frac{\partial^2}{\partial E^2}\ln\{ge^{-\beta E}\} \approx \frac{1}{k}\left.\frac{\partial^2 S}{\partial E^2}\right|_{E^*} \tag{7.129}$$

On the other hand, in general $S(E, V, N)$ obeys

$$\left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{1}{T} \Rightarrow \frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\left.\frac{1}{T}\right|_{N,V} = \left.\frac{\partial T}{\partial E}\right|_{N,V}\frac{\partial}{\partial T}\left.\frac{1}{T}\right|_{N,V} \tag{7.130}$$

this implies

$$\left.\frac{\partial^2 S}{\partial E^2}\right|_{E^*} = -\frac{\frac{1}{T^2}}{\left.\frac{\partial E}{\partial T}\right|_{N,V}} = -\frac{1}{T^2}\frac{1}{C_V} \tag{7.131}$$

Inserting this into Equations (7.128) or (7.129), we obtain (for $E^* = U$):

$$\ln\{ge^{-\beta E}\} = -\beta(U-TS) - \frac{1}{2kT^2C_V}(E-U)^2 + \cdots \tag{7.132}$$

or, after exponentiation,

$$p_c(E) \approx \frac{1}{Z}e^{-\beta(U-TS)}\exp\left\{-\frac{(E-U)^2}{2kT^2C_V}\right\} \tag{7.133}$$

The canonical energy distribution $p_c(E)$ in the vicinity of the most probable energy $E^* = \langle E\rangle = U$ is thus a Gaussian distribution, the width of which decreases at large particle numbers. The maximum value itself, $p_c(U)$, is $\frac{1}{Z}e^{-\beta F}$, with the free energy F. Now we see the profound reason for the equality of the results in the microcanonical and canonical ensembles: the deviations (fluctuations) of energy from the mean value in the canonical ensemble become smaller and smaller with increasing particle numbers. In the thermodynamic limit $N \to \infty$ they even vanish completely. This means that at a given temperature, the system can assume (up to very small deviations) only a certain energy, which coincides with the microcanonical total energy. As we have seen, the calculations in the canonical ensemble are much easier than those in the microcanonical one, and the latter is not often used for practical calculations. However, it is of considerable theoretical significance.

Virial theorem and equipartition theorem

In this section we want to make a statement on the mean energy $U = \langle E\rangle$ of a system at a given temperature T. Let $H(q_\nu, p_\nu)$ be the Hamiltonian of the system. All coordinates

q_ν and p_ν of phase space shall be denoted by x_i, where x_i runs over all momenta and coordinates ($i = 1, \ldots, 6N$). We want to calculate the mean value of the quantity $x_i \frac{\partial H}{\partial x_k}$, if x_i and x_k are two arbitrary coordinates or momenta:

$$\left\langle x_i \frac{\partial H}{\partial x_k} \right\rangle = \frac{1}{h^{3N}} \int d^{6N}x \rho(\vec{x}) x_i \frac{\partial H}{\partial x_k} \tag{7.134}$$

Here ρ can be the microcanonical, or alternatively, the canonical phase-space density; according to the preceding sections the results should be identical in both cases. At first we use Equation (7.134) in the microcanonical case, with

$$\rho_{mc}(\vec{x}) = \begin{cases} \dfrac{1}{\Omega} & E \leq H(\vec{x}) \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{7.135}$$

Inserting this into Equation (7.134), one obtains

$$\begin{aligned} \left\langle x_i \frac{\partial H}{\partial x_k} \right\rangle &= \frac{1}{\Omega h^{3N}} \int_{E \leq H(\vec{x}) \leq E + \Delta E} d^{6N}x x_i \frac{\partial H}{\partial x_k} \\ &= \frac{1}{\Omega h^{3N}} \int_{E \leq H(\vec{x}) \leq E + \Delta E} d^{6N}x x_i \frac{\partial (H - E)}{\partial x_k} \end{aligned} \tag{7.136}$$

because $\partial E / \partial x_k = 0$ (E is fixed). Now to this expression we apply the same trick which we have used before to calculate Ω,

$$\left\langle x_i \frac{\partial H}{\partial x_k} \right\rangle = \frac{1}{\Omega h^{3N}} \Delta E \frac{\partial}{\partial E} \int_{0 \leq H(\vec{x}) \leq E} d^{6N}x x_i \frac{\partial (H - E)}{\partial x_k} \tag{7.137}$$

i.e., first we integrate over all phase-space points below the energy surface and obtain the result for the thin energy shell of thickness ΔE by application of $\Delta E \frac{\partial}{\partial E}$. Integration by parts of the term $\partial (H - E)/\partial x_k$ yields

$$\begin{aligned} \left\langle x_i \frac{\partial H}{\partial x_k} \right\rangle = \frac{1}{\Omega h^{3N}} \Delta E \frac{\partial}{\partial E} \Bigg\{ &\int_{0 \leq H \leq E} d^{6N-1}x \, [x_i (H - E)]_{x_{k\,\min}}^{x_{k\,\max}} \\ &- \int_{0 \leq H \leq E} d^{6N}x (H - E) \frac{\partial x_i}{\partial x_k} \Bigg\} \end{aligned} \tag{7.138}$$

In the first term we still integrate over $6N - 1$ variables (without x_k). The quantities $x_{k\,\max}$ and $x_{k\,\min}$ need not be specified; they evolve in a unique way if the equation $E = H(\vec{x})$ is solved for x_k. For this reason the first term also vanishes, no matter whether x_k is a coordinate or a momentum. Namely, if x_k assumes its extreme value, the corresponding point lies on the energy surface which includes the integration region, and thus we have $H - E = 0$. Using $\partial x_i / \partial x_k = \delta_{ik}$, we obtain

$$\left\langle x_i \frac{\partial H}{\partial x_k} \right\rangle = -\frac{\delta_{ik}}{\Omega h^{3N}} \Delta E \frac{\partial}{\partial E} \int_{0 \leq H \leq E} d^{6N}x (H - E) \tag{7.139}$$

Here the differentiation $\partial / \partial E$ can be performed, if one takes care of the fact that the integration limits also depend on E. The general formula for the differentiation of an

integral, whose integrand and limits depend on a parameter α, is

$$\frac{\partial}{\partial\alpha}\int_{x=f(\alpha)}^{x=g(\alpha)} dx F(\alpha, x) = \int_{x=f(\alpha)}^{x=g(\alpha)} \frac{\partial F(\alpha, x)}{\partial\alpha} dx + \left[\frac{\partial g}{\partial\alpha} F(\alpha, g(\alpha)) - \frac{\partial f}{\partial\alpha} F(\alpha, f(\alpha))\right] \tag{7.140}$$

Applied to Equation (7.139), with $F \to (H - E)$ this yields

$$\left\langle x_i \frac{\partial H}{\partial x_k}\right\rangle = -\frac{\delta_{ik}}{\Omega h^{3N}} \Delta E\left\{\int_{0\le H\le E} d^{6N}x(-1) + \left[\frac{\partial E}{\partial E}(E - E) - 0(0 - E)\right]\right\} \tag{7.141}$$

$$\left\langle x_i \frac{\partial H}{\partial x_k}\right\rangle = \delta_{ik}\frac{\Delta E}{\Omega}\Sigma \tag{7.142}$$

because the integral in the curly brackets (with the factor h^{-3N}) just gives the total number of all states Σ in the interior of the energy surface. On the other hand, Ω was the number of states in a shell of thickness ΔE, so that $\Omega/\Delta E \approx g = \partial\Sigma/\partial E$ is the density of states.

$$\left\langle x_i \frac{\partial H}{\partial x_k}\right\rangle = \delta_{ik}\frac{\Sigma}{\frac{\partial\Sigma}{\partial E}} = \frac{\delta_{ik}}{\frac{\partial}{\partial E}\ln\Sigma} \tag{7.143}$$

As we have already noticed many times, for large particle numbers ($N \to \infty$) we have $\ln\Sigma \approx \ln\Omega$ (because $E^N \approx E^{N-1}$), so that $k \ln\Sigma$ may be replaced by the entropy, to very good approximation,

$$\left\langle x_i \frac{\partial H}{\partial x_k}\right\rangle = k\frac{\delta_{ik}}{\frac{\partial S}{\partial E}\Big|_{N,V}} = \delta_{ik}kT \tag{7.144}$$

This is the desired final result. First, it means that the expression $\left\langle x_i \frac{\partial H}{\partial x_k}\right\rangle$ has a non-zero mean value only for $i = k$. If x_i, for instance, is a coordinate q_ν, then according to Hamilton's equations of motion $\frac{\partial H}{\partial x_i} = \frac{\partial H}{\partial q_i} = -\dot{p}_i$:

$$\left\langle x_i \frac{\partial H}{\partial x_i}\right\rangle = -\langle q_i\dot{p}_i\rangle = -\langle q_i F_i\rangle = kT \tag{7.145}$$

In this case $\frac{\partial H}{\partial x_i}$ is just the generalized force F_i on the particle. Analogously, $x_i = p_i$ yields, with $\frac{\partial H}{\partial x_i} = \frac{\partial H}{\partial p_i} = \dot{q}_i$,

$$\left\langle x_i \frac{\partial H}{\partial x_i}\right\rangle = \langle p_i\dot{q}_i\rangle = kT \tag{7.146}$$

The quantity $p_i\dot{q}_i$ is just twice the kinetic energy in a certain direction, so that for a particle i which can move in three dimensions Equation (7.146) reads

$$\langle T_i\rangle = \frac{3}{2}kT \tag{7.147}$$

where T_i denotes the kinetic energy of particle i.

If Equation (7.145) is rewritten for vectors, correspondingly, we obtain

$$-\left\langle \vec{r}_i \cdot \vec{F}_i \right\rangle = 3kT \tag{7.148}$$

Therewith for N particles we obtain the *virial theorem*

$$\langle T \rangle = -\frac{1}{2}\left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i \right\rangle = \frac{3}{2} NkT \tag{7.149}$$

The second mean value (i.e., (Equation (7.148)) is called *Clausius' virial*: Just as Equation (7.147) is a measure of the mean kinetic energy, Clausius' virial is a measure of the mean potential energy. To understand this, we consider the case that the force F_i can be written as the gradient of a potential V,

$$-\left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i \right\rangle = \left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \nabla V_i \right\rangle \tag{7.150}$$

Assuming a power function $V \propto r^{\alpha}$ for the potential, we obtain

$$\langle \vec{r}_i \cdot \nabla V_i \rangle = \left\langle r \frac{\partial V_i}{\partial r} \right\rangle = \alpha \langle V_i \rangle \tag{7.151}$$

and thus according to Equation (7.149),

$$\langle T_i \rangle = \frac{\alpha}{2} \langle V_i \rangle = \frac{3}{2} kT \tag{7.152}$$

The virial is indeed proportional to the mean potential energy. Especially for quadratic potentials ($\alpha = 2$), in the mean the kinetic and potential energy are of equal magnitude and have the value $\frac{1}{2}kT$ per spatial direction. This statement can be formulated more generally for a Hamiltonian which contains only quadratic terms:

$$H = \sum_{\nu=1}^{3N} \left(A_\nu p_\nu^2 + B_\nu q_\nu^2 \right) \tag{7.153}$$

One can easily convince oneself that for such a Hamiltonian it holds that

$$2H = \sum_{\nu=1}^{3N} \left(p_\nu \frac{\partial H}{\partial p_\nu} + q_\nu \frac{\partial H}{\partial q_\nu} \right) \tag{7.154}$$

The mean value of the total energy is then

$$\langle H \rangle = \frac{1}{2} \left\{ \sum_{\nu=1}^{3N} \left\langle p_\nu \frac{\partial H}{\partial p_\nu} \right\rangle + \sum_{\nu=1}^{3N} \left\langle q_\nu \frac{\partial H}{\partial q_\nu} \right\rangle \right\} \tag{7.155}$$

If f is the number of quadratic terms in the Hamiltonian (here f is equal to $6N$), then by use of Equation (7.144) one obtains

$$\langle H \rangle = \frac{1}{2} fkT \tag{7.156}$$

In the literature f is often called the number of degrees of freedom of the system. However, this is a little confusing, since in classical mechanics the number of degrees of freedom is defined by the number of necessary coordinates, while strictly speaking, f counts the number of quadratic terms in Equation (7.153). However, if we keep the notation f, then Equation (7.156) reads:

In the mean each degree of freedom of the system at a temperature T has the thermal energy $\frac{1}{2}kT$.

This is the so-called *equipartition theorem* (equal distribution theorem), which says that the thermal energy is uniformly distributed over all degrees of freedom of the system. The equipartition theorem, of course, is a special case of the virial theorem for quadratic potentials.

We have obtained the virial theorem (7.149) with the aid of Equation (7.144) by taking a mean value over the ensembles; we have taken the mean value over all possible microstates of the microcanonical energy surface. However, the virial theorem can be directly derived from classical mechanics by taking a temporal mean value along the phase-space trajectory. This is thus one of the very scarce ways to check the equality of temporal mean values and ensemble mean values (ergodic theorem)! To do this, we start with the quantity

$$G = \sum_i \vec{p}_i \cdot \vec{r}_i \tag{7.157}$$

The total time derivative of G is

$$\frac{dG}{dt} = \sum_i \left(\dot{\vec{p}}_i \cdot \vec{r}_i + \vec{p}_i \cdot \dot{\vec{r}}_i \right) \tag{7.158}$$

Now we have, of course, $\sum_i \vec{p}_i \cdot \dot{\vec{r}}_i = 2T$ (here T denotes the kinetic energy) and $\dot{\vec{p}}_i = \vec{F}_i$, so that we obtain

$$\frac{dG}{dt} = \sum_i \vec{F}_i \cdot \vec{r}_i + 2T \tag{7.159}$$

Now we form the temporal mean value of Equation (7.159),

$$\overline{\frac{dG}{dt}} = \lim_{t \to \infty} \frac{1}{t} \int_0^t \frac{dG}{dt}\, dt \tag{7.160}$$

or

$$2\overline{T} + \overline{\sum_i \vec{r}_i \cdot \vec{F}_i} = \lim_{t \to \infty} \frac{1}{t} \{G(t) - G(0)\} \tag{7.161}$$

For a given total energy, $G(t)$ is a bounded function for all times, so that the limiting value on the right hand side is zero,

$$\overline{T} = -\frac{1}{2} \overline{\sum_i \vec{r}_i \cdot \vec{F}_i} \tag{7.162}$$

This is again the virial theorem (7.149), but now for temporal mean values instead of ensemble mean values. This correspondence is a direct hint that temporal mean values and ensemble mean values really provide equivalent results.

Now we still want to show that the mean value (7.134) and the result (7.144) can also be derived using the canonical phase-space density. To do this, we insert the canonical distribution

$$\rho_c(\vec{x}) = \frac{1}{Z} \exp\{-\beta H(\vec{x})\} \tag{7.163}$$

into Equation (7.134):

$$\left\langle x_i \frac{\partial H}{\partial x_k} \right\rangle = \frac{1}{Zh^{3N}} \int d^{6N}x e^{-\beta H} x_i \frac{\partial H}{\partial x_k} \tag{7.164}$$

Now the whole term $e^{-\beta H} \frac{\partial H}{\partial x_k} = -\frac{1}{\beta} \frac{\partial}{\partial x_k} e^{-\beta H}$ can be integrated by parts,

$$\left\langle x_i \frac{\partial H}{\partial x_k} \right\rangle = \frac{1}{Zh^{3N}} \left\{ \int d^{6N-1}x x_i \left[-\frac{1}{\beta} e^{-\beta H} \right]_{x_k \min}^{x_k \max} + \frac{\delta_{ik}}{\beta} \int d^{6N}x e^{-\beta H} \right\} \tag{7.165}$$

Here also, the first term must vanish. If, for instance, x_k is a momentum, then we have $x_{k\min} \to -\infty$ and $x_{k\max} \to +\infty$, so that the kinetic energy becomes very large and $e^{-\beta H} \to 0$. If x_k is a coordinate, then $x_{k\min}$ and $x_{k\max}$ lie on the walls of the container. However there the momenta are reversed (gases), so that the potential V becomes infinite and $e^{-\beta H} \to 0$. For oscillators (without a container), $x_{k\min} \to -\infty$ and $x_{k\max} \to +\infty$ is allowed, but then of course we also have $V \to \infty$ and $e^{-\beta H} \to 0$. The last integral in the curly bracket is (with the factor h^{-3N}) the partition function. Taking all this together, Equation (7.165) can be rewritten as

$$\left\langle x_i \frac{\partial H}{\partial x_k} \right\rangle = \frac{\delta_{ik}}{\beta} = \delta_{ik} kT \tag{7.166}$$

In the canonical case we therefore have the same result as in the microcanonical ensemble (7.144).

Example 7.13: The virial theorem and the ideal gas

Using the virial theorem one can easily derive the ideal gas law. This is very useful, especially for the equations of state of real gases. According to Equation (7.149), we have

$$-\left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i \right\rangle = 3NkT \tag{7.167}$$

Now the force $\vec{F}_i$ on a particle of the ideal gas is given exclusively by the momentum reversal at the container walls, and can therefore be expressed by the pressure of the gas. Denote by $d\vec{F}'$ the mean force which is exerted by all particles incident on a surface element $d\vec{S}$; i.e., $d\vec{F}' = p\, d\vec{S}$ (orientation of $d\vec{S}$ to the exterior). Then $d\vec{F} = -d\vec{F}' = -p\, d\vec{S}$ is the mean

force which is exerted by the piece $d\vec{S}$ of the container wall on the gas particles, and we have

$$\left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i \right\rangle = -p \oint \vec{r} \cdot d\vec{S} \tag{7.168}$$

This integral can be easily evaluated using Gauss' theorem,

$$-p \oint \vec{r} \cdot d\vec{S} = -p \int d^3r \, \mathrm{div}\, \vec{r} = -3p \int d^3r = -3pV \tag{7.169}$$

Inserting Equations (7.168) or (7.169) into (7.167), we immediately end up with

$$pV = NkT$$

For better understanding: canonical ensemble as the mean value of all possible distributions

In discussing the canonical ensemble we have been able to show that this ensemble exactly corresponds to the most probable distribution in phase space. Especially for the energy, we have even seen that the most probable energy value E^* in the canonical case is identical to the mean value $\langle E \rangle$ of all possible energies. The same can also be shown for the phase-space density itself. This is not only the most probable distribution, but also the mean value of all possible distributions. However, this proof is really not trivial.

Again we use the language of ensemble theory and consider $\mathcal{N}$ identical copies of the system. Let phase space be subdivided into equally large enumerated phase-space cells $\Delta\omega_i$. A distribution in phase space is then represented by the set $\{n_i\}$, if n_i is the number of systems which are in the microstate corresponding to $\Delta\omega_i$ ($\Delta\omega_i$ small). Of course, for all distributions $\{n_i\}$ it must hold that

$$\mathcal{N} = \sum_i n_i \tag{7.170}$$

if i runs over all phase-space cells. Another condition the set $\{n_i\}$ must fulfill is

$$\mathcal{N}U = \sum_i n_i E_i \tag{7.171}$$

i.e., the mean value of all energies E_i over all phase-space cells i must be equal to the mean energy U. For every distribution $\{n_i\}$ which is compatible with Equations (7.170) and (7.171), there are still another $W\{n_i\}$ ways to reorder the distribution, which we also know already,

$$W\{n_i\} = \frac{\mathcal{N}!}{\prod_i n_i!} \tag{7.172}$$

The mean distribution $\langle\{n_i\}\rangle$ is just given by the set of mean values of the $\langle n_i \rangle$,

$$\langle n_i \rangle = \frac{\sum''_{\{n_i\}} n_i W\{n_i\}}{\sum''_{\{n_i\}} W\{n_i\}} \tag{7.173}$$

Here the sum extends over all possible distributions $\{n_i\}$, where the double prime at the sum indicates that only such distributions are considered which fulfill the boundary conditions (7.170) *and* (7.171). Of course, $W\{n_i\}$ is proportional to the probability of finding the special distribution $\{n_i\}$. The denominator in Equation (7.173) guarantees normalization. Equation (7.173) can be rewritten with the aid of a little trick.

At first we introduce a new $\tilde{W}$ instead of W,

$$\tilde{W}\{n_i\} = \mathcal{N}! \prod_i \frac{\omega_i^{n_i}}{n_i!} \tag{7.174}$$

Here the ω_i shall be arbitrary numbers. Of course, for $\omega_i = 1$, $\tilde{W}$ goes over into W. Now $\tilde{W}$ allows us to write Equation (7.173) in a more convenient way. If one forms

$$\Gamma(\mathcal{N}, U) = \sum_{\{n_i\}}'' \tilde{W}\{n_i\} \tag{7.175}$$

one has

$$\langle n_i \rangle = \omega_i \frac{\partial}{\partial \omega_i} \ln \Gamma \Big|_{\text{all } \omega_i = 1} \tag{7.176}$$

In the course of performing the differentiation in Equation (7.176), Γ just comes into the denominator and the factor n_i into the numerator, where the ω_is cancel if all $\omega_i = 1$. The quantity $\Gamma(\mathcal{N}, U)$ is a function of $\mathcal{N}$ and U due to the boundary conditions (7.170) and (7.171). Therefore, it is sufficient to calculate

$$\Gamma(\mathcal{N}, U) = \mathcal{N}! \sum_{\{n_i\}}'' \prod_i \left(\frac{\omega_i^{n_i}}{n_i!} \right) \tag{7.177}$$

Now $\Gamma(\mathcal{N}, U)$ would simply be $(\omega_1 + \omega_2 + \cdots)^{\mathcal{N}}$, according to the polynomial theorem, if we did not have the energy condition (7.171).

We can use a trick for the calculation, which we already know from the Laplace transformation. We calculate the Laplace transform of $\Gamma(\mathcal{N}, U)$ with respect to U,

$$G(\mathcal{N}, \beta) = \int_0^\infty dU \exp\{-\beta \mathcal{N} U\} \Gamma(\mathcal{N}, U) \tag{7.178}$$

Here β is an arbitrary complex variable, which however must have the dimensions of (energy)$^{-1}$. The quantity $G(\mathcal{N}, \beta)$ can be calculated for arbitrary β. Inserting Equation (7.177) into Equation (7.178), we obtain

$$G(\mathcal{N}, \beta) = \int_0^\infty dU \sum_{\{n_i\}}'' \frac{\mathcal{N}!}{n_1! n_2! \cdots} \omega_1^{n_1} \omega_2^{n_2} \cdots \exp\{-\beta \mathcal{N} U\} \tag{7.179}$$

Due to the boundary condition (7.171) for the sum in Equation (7.10), in the exponential function $\mathcal{N}U$ may be replaced by $\sum_i n_i E_i$:

$$G(\mathcal{N}, \beta) = \int_0^\infty dU \sum_{\{n_i\}}'' \frac{\mathcal{N}!}{n_1! n_2! \cdots} \left(\omega_1 e^{-\beta E_1}\right)^{n_1} \left(\omega_2 e^{-\beta E_2}\right)^{n_2} \cdots \tag{7.180}$$

The double-primed sum in Equation (7.180) extends only over distributions $\{n_i\}$ having the fixed mean energy $\mathcal{N}U$. However, since then the whole expression must be integrated over all energies U, we can equally well drop the integration $\int dU$ and instead perform the sum *without* the energy condition,

$$G(\mathcal{N}, \beta) = \sum_{\{n_i\}}'' \frac{\mathcal{N}!}{n_1! n_2! \cdots} \left(\omega_1 e^{-\beta E_1}\right)^{n_1} \left(\omega_2 e^{-\beta E_2}\right)^{n_2} \cdots \tag{7.181}$$

where the single prime indicates that the sum is now only restricted by the normalization (7.170). Then the polynomial theorem can be applied to Equation (7.181), with the result

$$G(\mathcal{N}, \beta) = \left[\sum_i \omega_i e^{-\beta E_i}\right]^{\mathcal{N}} \tag{7.182}$$

The reason for the Laplace transformation, which at first seems to be unmotivated, is the fact that we can calculate Γ from $G(\mathcal{N}, \beta)$ by the reverse transformation

$$\Gamma(\mathcal{N}, U) = \frac{1}{2\pi i} \int_{\beta'-i\infty}^{\beta'+i\infty} d\beta e^{\beta \mathcal{N} U} G(\mathcal{N}, \beta) \tag{7.183}$$

which is what we originally intended to do. Therefore we must examine the integrand of Equation (7.183) in a little more detail:

$$I_{\mathcal{N}}(\beta) = e^{\beta \mathcal{N} U} G(\mathcal{N}, \beta) = \left[\sum_i \omega_i \exp\{\beta(U - E_i)\}\right]^{\mathcal{N}} \tag{7.184}$$

To do this, we abbreviate

$$f(\beta) = \sum_i \omega_i \exp\{\beta(U - E_i)\} \Rightarrow I_{\mathcal{N}}(\beta) = [f(\beta)]^{\mathcal{N}} \tag{7.185}$$

At first we study $I_{\mathcal{N}}(\beta)$ on the real β-axis. The factor $(e^{\beta U})^{\mathcal{N}}$ increases extremely rapidly with β for large $\mathcal{N}$ ($\beta U > 0$). On the contrary, $G(\mathcal{N}, \beta)$ decreases equally rapidly with β due to the factors $e^{-\beta E_i}$. Since both terms are strictly monotonous, $I_{\mathcal{N}}(\beta)$ must have a very sharp extremum for some real β_0, where β_0 must be determined from

$$\frac{\partial}{\partial \beta} I_{\mathcal{N}}(\beta)\bigg|_{\beta_0} = \mathcal{N}[f(\beta_0)]^{\mathcal{N}-1} \sum_i \omega_i (U - E_i) \exp\{\beta_0(U - E_i)\} = 0 \tag{7.186}$$

Since the factor in the square bracket is positive, the condition for β_0, which thus has to be determined from U, reads

$$U = \frac{\sum_i \omega_i E_i e^{-\beta_0 E_i}}{\sum_i \omega_i e^{-\beta_0 E_i}} \tag{7.187}$$

Recall that the ω_i are only formal parameters (which later on will all be set equal to one). The sharpness of the minimum can be estimated with the aid of the second derivative:

$$\frac{\partial^2}{\partial \beta^2} I_{\mathcal{N}}(\beta) = \mathcal{N}(\mathcal{N} - 1)[f(\beta)]^{\mathcal{N}-2} \left(\sum_i \omega_i (U - E_i) \exp\{\beta(U - E_i)\}\right)^2$$

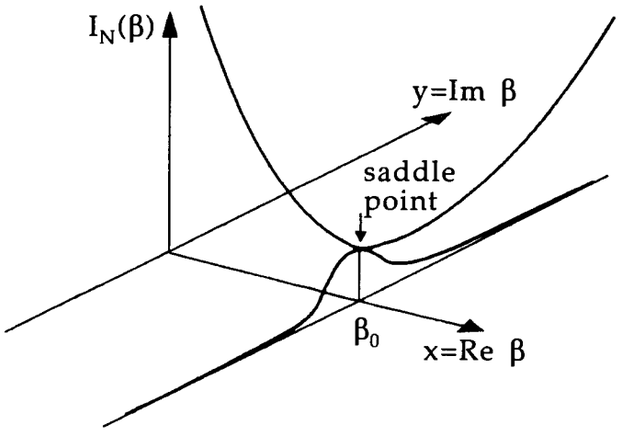


Figure 7.12. The function $I_{\mathcal{N}}(\beta)$.

$$+\mathcal{N}[f(\beta)]^{\mathcal{N}-1}\left(\sum_i \omega_i\,(U-E_i)^2\exp\{\beta(U-E_i)\}\right) \tag{7.188}$$

or

$$\left.\frac{\partial^2}{\partial\beta^2}I_{\mathcal{N}}(\beta)\right|_{\beta_0} = \mathcal{N}[f(\beta_0)]^{\mathcal{N}}\,\frac{\sum_i \omega_i\,(U-E_i)^2\,e^{-\beta_0 E_i}}{\sum_i \omega_i e^{-\beta_0 E_i}} \tag{7.189}$$

since the first term in Equation (7.188) vanishes at β_0 (because of Equation (7.187)), and because in the second term $e^{\beta U}$ cancels after drawing out $f(\beta_0)$. Now $f(\beta_0)$ is greater than zero (as one can easily convince oneself), as well as the last factor in Equation (7.188), which can be interpreted as $\langle(U-E_i)^2\rangle$. (This is the reason that we indeed deal with a minimum.) The whole expression is therefore very large for $\mathcal{N}\to\infty$, and the minimum becomes arbitrarily sharp.

Next we examine the behavior of $I_{\mathcal{N}}(\beta)$ in β_0 in the direction of the imaginary β-axis. A short consideration reveals that $I_{\mathcal{N}}(\beta)$ must have a sharp maximum here, so that β_0 forms a saddle point of $I_{\mathcal{N}}(\beta)$:

One recognizes at once that the complex function $I_{\mathcal{N}}(\beta)$ at the point $\beta_0 = \Re(\beta_0)+i\cdot 0$ is complex differentiable, and that therefore the Cauchy-Riemann differential equations are fulfilled:

$$\frac{\partial}{\partial x}U = \frac{\partial}{\partial y}V \qquad \text{and} \qquad \frac{\partial}{\partial y}U = -\frac{\partial}{\partial x}V \tag{7.190}$$

where $\beta = x+iy$, $U=\Re(I_{\mathcal{N}})$ and $V=\Im(I_{\mathcal{N}})$. Partial differentiation yields:

$$\frac{\partial^2}{\partial x^2}\Re I(\beta) = -\frac{\partial^2}{\partial y^2}\Re I(\beta) \tag{7.191}$$

Hence, if $I_{\mathcal{N}}(\beta)$ has a minimum at β_0 on the real axis, then on the imaginary axis it must have a maximum at β_0. This maximum is as sharp as the minimum.

Taking all this together, the integral (7.183) can now be calculated very conveniently, if the integration path (which runs arbitrarily parallel to the $\Im\beta$-axis) is laid through β_0. There the contribution to the integral comes practically exclusively from this sharp maximum.

It is therefore convenient to approximate the integrand on the integration path by a Gaussian. We set

$$I_{\mathcal{N}}(\beta) = [f(\beta)]^{\mathcal{N}} = [\exp\{g(\beta)\}]^{\mathcal{N}} \tag{7.192}$$

with a new function $g(\beta)$,

$$g(\beta) = \ln f(\beta) \tag{7.193}$$

The reason for this substitution is that f changes very strongly with $\Im(\beta)$, but g, which is the logarithm of f, changes much more moderately with $\Im(\beta)$. Therefore we can expand g around β_0 for small $y = \Im\beta$, $\beta = \beta_0 + iy$,

$$g(\beta) = g(\beta_0) + g'(\beta_0)iy - \frac{1}{2}g''(\beta_0)y^2 + \cdots \tag{7.194}$$

Now we have

$$g'(\beta_0) = \frac{f'(\beta_0)}{f(\beta_0)} = 0 \tag{7.195}$$

because $f'(\beta_0) = 0$, and therefore by inserting Equation (7.194) into Equation (7.192) we get

$$I_{\mathcal{N}}(\beta) = [f(\beta_0)]^{\mathcal{N}} \exp\left\{-\frac{\mathcal{N}}{2}g''(\beta_0)y^2\right\} \tag{7.196}$$

Here β_0 is the fixed value of the saddle point. With $d\beta \to i\,dy$, Equation (7.183) is rewritten as

$$\Gamma(\mathcal{N}, U) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dy[f(\beta_0)]^{\mathcal{N}} \exp\left\{-\frac{\mathcal{N}}{2}g''(\beta_0)y^2\right\} \tag{7.197}$$

The value of this Gaussian integral can be easily written down,

$$\Gamma(\mathcal{N}, U) = [f(\beta_0)]^{\mathcal{N}}[2\pi\mathcal{N}g''(\beta_0)]^{-1/2} \tag{7.198}$$

Here we must insert

$$f(\beta_0) = \sum_i \omega_i \exp\{\beta_0(U - E_i)\} \tag{7.199}$$

and

$$\begin{aligned} g''(\beta_0) &= \frac{f''(\beta_0)}{f(\beta_0)} - \left(\frac{f'(\beta_0)}{f(\beta_0)}\right)^2 \\ &= \frac{f''(\beta_0)}{f(\beta_0)} = \frac{\sum_i \omega_i (U - E_i)^2 \exp\{\beta_0(U - E_i)\}}{\sum_i \omega_i \exp\{\beta_0(U - E_i)\}} \end{aligned} \tag{7.200}$$

We obtain for $\ln \Gamma$, using Equation (7.198),

$$\ln \Gamma(\mathcal{N}, U) = \mathcal{N} \ln f(\beta_0) - \frac{1}{2} \ln \left\{ 2\pi \mathcal{N} \frac{f''(\beta_0)}{f(\beta_0)} \right\} \approx \mathcal{N} \ln f(\beta_0) \tag{7.201}$$

Here we have neglected the second term in the limit $\mathcal{N} \to \infty$, because it grows only logarithmically with $\mathcal{N}$. Now we can calculate the mean distribution $\langle n_i \rangle$ according to Equation (7.176):

$$\langle n_i \rangle = \omega_i \frac{\partial}{\partial \omega_i} \ln \Gamma \Big|_{\text{all } \omega_i = 1} = \mathcal{N} \left. \frac{\omega_i \exp\{\beta_0 (U - E_i)\}}{\sum_j \omega_j \exp\{\beta_0 (U - E_j)\}} \right|_{\text{all } \omega = 1} \tag{7.202}$$

$$p_i = \frac{\langle n_i \rangle}{\mathcal{N}} = \frac{e^{-\beta_0 E_i}}{\sum_j e^{-\beta_0 E_j}} \tag{7.203}$$

The point β_0 must be determined from Equation (7.187) with $\omega_i = 1$. Strictly speaking, in the derivative $\partial / \partial \omega_i$ in Equation (7.202) we would have to take into account that the value of β_0 depends on ω_i, so that according to the chain rule a term $\omega_i \frac{\partial \beta_0}{\partial \omega_i} \frac{\partial}{\partial \beta_0} \ln \Gamma$ also appears; because of $f'(\beta_0) = 0$, however, this term must be equal to zero in accordance with Equation (7.201).

With Equations (7.203) and (7.187) ($\omega_i = 1$) the mean distribution of the $\mathcal{N}$ identical systems on the microstate i is completely identical to the most probable distribution (7.20). Indeed, the results (7.203) and (7.201) are even more useful. Namely, now we can even denote the fluctuations in each single microstate i, i.e., the deviations from the mean distribution (7.203). Up to now, we have only been able to do this for the deviations from the mean energy $\langle E \rangle = U$, and we have noticed that the relative deviation becomes smaller with increasing $\mathcal{N}$. This is also true for each single microstate: The standard deviation

$$\left\langle (\Delta n_i)^2 \right\rangle = \left\langle n_i^2 \right\rangle - \langle n_i \rangle^2 = \left(\omega_i \frac{\partial}{\partial \omega_i} \right) \left(\omega_i \frac{\partial}{\partial \omega_i} \right) \ln \Gamma \Big|_{\omega_i = 1} \tag{7.204}$$

is a measure for the fluctuations in the microstate i. That Equation (7.204) is correct can be seen in the following way:

$$\begin{aligned}
\left(\omega_i \frac{\partial}{\partial \omega_i} \right) \left(\omega_i \frac{\partial}{\partial \omega_i} \ln \Gamma \right) &= \omega_i \frac{\partial}{\partial \omega_i} \ln \Gamma + \omega_i^2 \frac{\partial}{\partial \omega_i} \frac{1}{\Gamma} \frac{\partial \Gamma}{\partial \omega_i} \\
&= \langle n_i \rangle + \omega_i^2 \left\{ -\frac{1}{\Gamma^2} \left(\frac{\partial \Gamma}{\partial \omega_i} \right)^2 + \frac{1}{\Gamma} \frac{\partial^2 \Gamma}{\partial \omega_i^2} \right\} \\
&= \langle n_i \rangle - \left(\frac{\omega_i}{\Gamma} \frac{\partial \Gamma}{\partial \omega_i} \right)^2 + \frac{\omega_i^2}{\Gamma} \frac{\partial^2 \Gamma}{\partial \omega_i^2} \\
&= \langle n_i \rangle - \langle n_i \rangle^2 + \frac{1}{\Gamma} \sum_{\{n_i\}}'' n_i (n_i - 1) \mathcal{N}! \prod_i \frac{\omega_i^{n_i}}{n_i!} \\
&= \langle n_i \rangle - \langle n_i \rangle^2 + \left\langle n_i^2 \right\rangle - \langle n_i \rangle \\
&= \left\langle n_i^2 \right\rangle - \langle n_i \rangle^2
\end{aligned} \tag{7.205}$$

With Equation (7.202), Equation (7.204) becomes

$$\langle(\Delta n_i)^2\rangle = \mathcal{N}\omega_i \frac{\partial}{\partial \omega_i}\left[\frac{\omega_i \exp\{\beta_0(U-E_i)\}}{\sum_j \omega_j \exp\{\beta_0(U-E_j)\}}\right]\Bigg|_{\text{all } \omega_i=1} \tag{7.206}$$

Here, as in Equation (7.202), β_0 is strictly speaking a function of the ω_i and thus

$$\begin{aligned}\frac{\langle(\Delta n_i)^2\rangle}{\mathcal{N}} = {} & \frac{\omega_i \exp\{\beta_0(U-E_i)\}}{\sum_j \omega_j \exp\{\beta_0(U-E_j)\}} - \left(\frac{\omega_i \exp\{\beta_0(U-E_i)\}}{\sum_j \omega_j \exp\{\beta_0(U-E_j)\}}\right)^2 \\ & + \frac{\partial\beta_0}{\partial\omega_i}\left\{\frac{\omega_i^2(U-E_i)\exp\{\beta_0(U-E_i)\}}{\sum_j \omega_j \exp\{\beta_0(U-E_j)\}}\right. \\ & \left. - \frac{\sum_j \omega_j(U-E_j)\exp\{\beta_0(U-E_j)\}}{\left(\sum_j \omega_j \exp\{\beta_0(U-E_j)\}\right)^2}\omega_i^2 \exp\{\beta_0(U-E_i)\}\right\}\end{aligned} \tag{7.207}$$

The last term is, of course, equal to zero because of Equation (7.187). Cancelling all factors $\exp\{\beta_0 U\}$, and inserting Equation (7.202), one obtains (with $\omega_i = 1$ for all i)

$$\frac{\langle(\Delta n_i)^2\rangle}{\mathcal{N}} = \frac{\langle n_i\rangle}{\mathcal{N}} - \left(\frac{\langle n_i\rangle}{\mathcal{N}}\right)^2 + \frac{\partial\beta_0}{\partial\omega_i}(U-E_i)\frac{\langle n_i\rangle}{\mathcal{N}} \tag{7.208}$$

The derivative $\partial\beta_0/\partial\omega_i$ follows easily by differentiation of Equation (7.187) with respect to ω_i. The energy U is fixed, and therefore we have

$$\begin{aligned}\frac{\partial U}{\partial\omega_i} = 0 = {} & \frac{E_i \exp\{-\beta_0 E_i\}}{\sum_j \omega_j \exp\{-\beta_0 E_j\}} - \frac{\sum_j \omega_j E_j \exp\{-\beta_0 E_j\}}{\left(\sum_j \omega_j \exp\{-\beta_0 E_j\}\right)^2}\exp\{-\beta_0 E_i\} \\ & + \frac{\partial\beta_0}{\partial\omega_i}\left\{-\frac{\sum_j \omega_j E_j^2 \exp\{-\beta_0 E_j\}}{\sum_j \omega_j \exp\{-\beta_0 E_j\}}\right. \\ & \left. + \frac{\left(\sum_j \omega_j E_j \exp\{-\beta_0 E_j\}\right)^2}{\left(\sum_j \omega_j \exp\{-\beta_0 E_j\}\right)^2}\right\}\end{aligned} \tag{7.209}$$

or, for $\omega_i = 1$, if Again equation (7.202) is inserted (observe Equation (7.187)),

$$\frac{\partial\beta_0}{\partial\omega_i} = \frac{E_i - U}{\langle E_i^2\rangle - U^2}\frac{\langle n_i\rangle}{\mathcal{N}} \tag{7.210}$$

If we insert this into Equation (7.208), we finally get

$$\frac{\langle(\Delta n_i)^2\rangle}{\mathcal{N}} = \frac{\langle n_i\rangle}{\mathcal{N}}\left[1 - \frac{\langle n_i\rangle}{\mathcal{N}} - \frac{(E_i-U)^2}{\langle(E_i-U)^2\rangle}\frac{\langle n_i\rangle}{\mathcal{N}}\right] \tag{7.211}$$

because $\langle (E_i - U)^2 \rangle = \langle E_i^2 - 2E_iU + U^2 \rangle = \langle E_i^2 \rangle - \langle 2E_i \rangle U + U^2 = \langle E_i^2 \rangle - U^2$. Using this, the relative fluctuations are calculated to be

$$\frac{\langle (\Delta n_i)^2 \rangle}{\langle n_i \rangle^2} = \frac{1}{\langle n_i \rangle} - \frac{1}{\mathcal{N}} \left[1 + \frac{(E_i - U)^2}{\langle (E_i - U)^2 \rangle} \right] \tag{7.212}$$

For $\mathcal{N} \to \infty$, all $\langle n_i \rangle \to \infty$, and the relative fluctuation in the microstate i vanishes. In other words: Not only is the mean energy in the canonical ensemble identical to the most probable energy, and not only does t correspond to the energy which is given in the microcanonical ensemble, but the phase-space density is also simultaneously the mean and the most probable distibution of all possible distributions. The deviations (fluctuations) of this distribution vanish for a large number of systems ($\mathcal{N} \to \infty$).

8 Applications of Boltzmann Statistics

Quantum Systems in Boltzmann Statistics

In this chapter we want to show how what we have learned up to now can also be applied to quantum mechanical systems. However, this is not a truly quantum statistical consideration which takes into account the indistinguishability of the quantum mechanical particles. Those considerations will be introduced in part III of this book. However, some important statements which also remain true in quantum statistics can already be derived with the aid of the canonical distribution. This shall be demonstrated for the example of a set of N quantum mechanical harmonic oscillators. The energy eigenvalues of a quantum mechanical harmonic oscillator are well-known from Volume 4 of this series:

$$\epsilon_n = \hbar\omega\left(n + \frac{1}{2}\right), \qquad n = 0, 1, 2, \ldots \tag{8.1}$$

They are determined by a quantum number n which can assume all numbers 0, 1, 2, ... Now we must translate the classical canonical phase-space density (for an oscillator),

$$\rho(q, p) = \frac{\exp\{-\beta H(q, p)\}}{Z(T, V, 1)}$$

$$Z(T, V, 1) = \frac{1}{h}\int dq \int dp \exp\{-\beta H(q, p)\} \tag{8.2}$$

to the quantum mechanical case. As we had already noticed in the case of the ideal gas, the role of the microstate (q, p) in quantum mechanics is taken over by the quantum numbers. Therefore we set

$$\rho_n = \frac{\exp\{-\beta\epsilon_n\}}{Z(T, V, 1)}$$

$$Z(T, V, 1) = \sum_n \exp\{-\beta\epsilon_n\} \tag{8.3}$$

Now the microstates of the oscillator are really discretely enumerated with the aid of the quantum numbers. The quantity ρ_n is the probability for an oscillator to be in a quantum

state with the quantum number n. If an oscillator has several quantum numbers, then of course the index number must be extended. Instead of the classical energy $H(q, p)$ we now have the energy eigenvalue ϵ_n belonging to the microstate n. Equations (8.3) are correspondingly valid for many-body systems, too. For noninteracting systems we have, again (the particles are taken to be distinguishable),

$$Z(T, V, N) = [Z(T, V, 1)]^N \tag{8.4}$$

because the many-particle states result from the occupation of the single-particle states with N particles, and the total energy is the sum of all single-particle energies,

$$E_{n_1,n_2,\ldots,n_N} = \epsilon_{n_1} + \epsilon_{n_2} + \cdots + \epsilon_{n_N} \tag{8.5}$$

where particle 1 occupies the quantum state n_1, particle 2 occupies n_2, etc. However, as we have already mentioned several times, this is not yet quantum statistics, since we still consider the particles to be enumerable.

For distinguishable particles we have

$$\begin{aligned} Z(T, V, N) &= \sum_{n_1,n_2,\ldots,n_N} \exp\left\{-\beta \sum_i \epsilon_{n_i}\right\} \\ &= \sum_{n_1} \exp\{-\beta\epsilon_{n_1}\} \cdots \sum_{n_N} \exp\{-\beta\epsilon_{n_N}\} \\ &= [Z(T, V, 1)]^N \end{aligned} \tag{8.6}$$

and the Gibbs factor $1/N!$ is added afterwards for indistinguishable particles. This ad hoc prescription still is a real conceptional problem that will not be removed before the introduction of a quantum statistical manner of counting the microstates.

As usual, the partition function for quantum systems yields the thermodynamic properties with the aid of the free energy F,

$$F(T, V, N) = -kT \ln Z(T, V, N) \tag{8.7}$$

Now we want to apply these considerations to a system of N quantum mechanical harmonic oscillators:

Example 8.1: N quantum mechanical harmonic oscillators

The single-particle partition function of the system is

$$\begin{aligned} Z(T, V, 1) &= \sum_n \exp\{-\beta\epsilon_n\} = \sum_{n=0}^{\infty} \exp\left\{-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right\} \\ &= \exp\left\{-\frac{\beta\hbar\omega}{2}\right\} \sum_{n=0}^{\infty} (\exp\{-\beta\hbar\omega\})^n \end{aligned}$$

This geometrical series can be easily calculated,

$$Z(T, V, 1) = \frac{\exp\left\{-\frac{\beta\hbar\omega}{2}\right\}}{1 - \exp\{-\beta\hbar\omega\}} = \frac{1}{\exp\left\{\frac{\beta\hbar\omega}{2}\right\} - \exp\left\{-\frac{\beta\hbar\omega}{2}\right\}}$$

$$= \left[2 \sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-1} \tag{8.8}$$

The N-particle partition function results from this as

$$Z(T, V, N) = [Z(T, V, 1)]^N = \left[2 \sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-N} \tag{8.9}$$

Here we do not need any Gibbs factor, if we consider the oscillators to be distinguishable, analogous to the classical case. The free energy is

$$F(T, V, N) = NkT \ln\left\{2 \sinh\left(\frac{\beta\hbar\omega}{2}\right)\right\} = \frac{N}{2}\hbar\omega + NkT \ln\{1 - \exp\{-\beta\hbar\omega\}\}$$

The term $N\hbar\omega/2$ is exactly the contribution of the zero-point energy of N oscillators to the total energy. Additional thermodynamic properties can be derived immediately,

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = \frac{F}{N}$$

$$p = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = 0$$

Just as with classical oscillators, the quantum mechanical oscillators do not exert any pressure, because they are not capable of translational motion. The entropy is

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = Nk\left[\frac{\beta\hbar\omega}{2} \coth\left(\frac{\beta\hbar\omega}{2}\right) - \ln\left\{2 \sinh\left(\frac{\beta\hbar\omega}{2}\right)\right\}\right]$$

$$= Nk\left[\frac{\beta\hbar\omega}{\exp\{\beta\hbar\omega\} - 1} - \ln\{1 - \exp\{-\beta\hbar\omega\}\}\right] \tag{8.10}$$

and the internal energy is $U = F + TS$,

$$U = N\hbar\omega\left[\frac{1}{2} + \frac{1}{\exp\{\beta\hbar\omega\} - 1}\right] \tag{8.11}$$

Again, the first term is just the zero-point energy. Equation (8.11) is of great importance. Namely, it can be interpreted to mean that U equals N times the mean energy of *one* oscillator,

$$U = N\langle\epsilon_n\rangle \qquad \text{with} \quad \langle\epsilon_n\rangle = \hbar\omega\left[\frac{1}{2} + \frac{1}{\exp\{\beta\hbar\omega\} - 1}\right]$$

Comparing this with Equation (8.1), the quantity

$$\langle n\rangle = \frac{1}{\exp\{\beta\hbar\omega\} - 1} \qquad \text{for} \quad \langle\epsilon_n\rangle = \hbar\omega\left(\frac{1}{2} + \langle n\rangle\right) \tag{8.12}$$

is obviously the mean quantum number $\langle n\rangle$, i.e., the mean level of excitation of an oscillator at temperature T. This result remains correct also in quantum statistics! In addition, one can see

that the equipartition theorem is *not* valid for the quantum mechanical oscillators. The latter states for N classical oscillators (as already calculated)

$$U_{\mathrm{cl}} = NkT \tag{8.13a}$$

Of course, Equation (8.12) can also be calculated directly, since it is valid that

$$\begin{aligned}\langle \epsilon_n \rangle &= \frac{1}{Z}\sum_{n=0}^{\infty} \epsilon_n e^{-\beta\epsilon_n} = \frac{1}{Z}\sum_{n=0}^{\infty} \hbar\omega(n+\frac{1}{2})e^{-\beta\epsilon_n} \\ &= \frac{\hbar\omega}{Z}\cdot\left\{\sum_{n=0}^{\infty} n e^{-\beta\epsilon_n} + \frac{1}{2}\sum_{n=0}^{\infty} e^{-\beta\epsilon_n}\right\}\end{aligned}$$

The second sum yields $\frac{1}{2}Z$, and the first sum is equal to

$$\sum_{n=0}^{\infty} n e^{-\beta\hbar\omega[n+\frac{1}{2}]} = e^{-\frac{\beta\hbar\omega}{2}}\sum_{n=0}^{\infty} n\left(e^{-\beta\hbar\omega}\right)^n = e^{-\frac{\beta\hbar\omega}{2}}\cdot\frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}$$

Thus, the mean energy follows as

$$\langle \epsilon_n \rangle = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{Z}\cdot e^{-\frac{\beta\hbar\omega}{2}}\cdot\frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}$$

Inserting for Z the first term of Equation (8.8) we obtain Equation (8.12). To reveal the connection between the classical result (8.13a) and the quantum mechanical one (8.11), we expand the exponential function in Equation (8.11) for the limiting case of high temperatures $T \to \infty, \beta\hbar\omega \to 0$,

$$\begin{aligned}U &= \frac{N}{2}\hbar\omega + N\hbar\omega\left[\frac{1}{(1+\beta\hbar\omega+\frac{1}{2}(\beta\hbar\omega)^2+\cdots)-1}\right] \\ &\approx \frac{N}{2}\hbar\omega + N\hbar\omega\left[\frac{1}{\beta\hbar\omega(1+\frac{1}{2}\beta\hbar\omega+\cdots)}\right] \\ &\approx \frac{N}{2}\hbar\omega + \frac{N}{\beta}\left(1-\frac{1}{2}\beta\hbar\omega+\cdots\right) \\ &\approx NkT+\cdots\end{aligned} \tag{8.13}$$

In the case of high temperatures the classical limit is exactly recovered. This is easily understood, because the characteristic parameter $\beta\hbar\omega = \hbar\omega/kT$ measures the ratio of the energy levels of the oscillator compared to the mean thermal energy kT which is available. If the latter is very large, the discrete structure of the energy spectrum does not show up any more, and one has the classical limit. On the other hand, for the case $T \to 0$ or $\beta\hbar\omega \to \infty$, one has the largest deviations from the classical case. Then

$$U \approx \frac{N}{2}\hbar\omega$$

In Figure 8.1 the mean energy per oscillator is shown in units of $\hbar\omega$. Curve 1 is the correct quantum mechanical result. For $T = 0$ there remains the zero-point energy $\hbar\omega/2$, while for $T \to \infty$ the classical case $\propto kT$ (curve 2) is approached. Curve 3 corresponds to the original Planck oscillator.

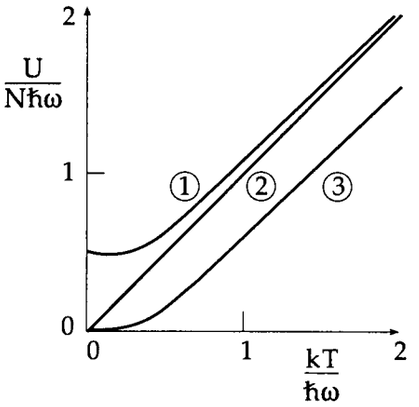


Figure 8.1. Mean energy per oscillator.

Around 1900, Planck became the first to assume discrete energy levels for oscillators in connection with the thermal radiation of a blackbody. In contrast to Equation (8.1), however, he had no zero-point energy (cf. Example 2.2 of *Quantum Mechanics: An Introduction*). This led to the result that in the case of high temperatures the oscillator also did *not* reproduce the classical result.

This contradiction was not removed until 1924, when the Schrödinger equation was established, which automatically provides the zero-point energy.

The heat capacity of the quantum mechanical oscillators in the case of low temperatures also shows strong deviations from the classical value (cf. Equation (6.63))

$$C_V^{\mathrm{cl}} = C_p^{\mathrm{cl}} = Nk$$

while now

$$C_V = \left.\frac{\partial U}{\partial T}\right|_{N,V} = Nk(\beta\hbar\omega)^2 \frac{\exp\{\beta\hbar\omega\}}{(\exp\{\beta\hbar\omega\} - 1)^2} \tag{8.14}$$

By an expansion analogous to Equation (8.13), one can check that for $\beta\hbar\omega \to 0$, $C_V \to C_V^{\mathrm{cl}}$ converges, as it should be. However, for small temperatures, $\beta\hbar\omega \to \infty$, C_V approaches zero like $x^2 e^{-x} (x \to \infty)$! This is also at once clear, if we consider the following: If the thermal energy is $kT \ll \hbar\omega$, then an oscillator cannot (only with extremely small probability) be excited to a higher energy level. The system is thus not at all capable of absorbing the energy kT offered by the heat bath.

On the other hand, the classical system can absorb arbitrarily small energies kT. The fact that the heat capacity vanishes for small temperatures is characteristic for all quantum systems with a discrete spectrum. (See Figure 8.2.)

It is very instructive to calculate from the partition function (8.9) the corresponding density of states of the N-oscillator system. To do this, for

$$Z(T, V, N) = \left[\frac{\exp\{-\frac{1}{2}\beta\hbar\omega\}}{1 - \exp\{-\beta\hbar\omega\}}\right]^N$$

with the aid of the binomial expansion

$$\frac{1}{(1-x)^N} = \sum_{l=0}^{\infty} \binom{-N}{l} (-1)^l x^l = \sum_{l=0}^{\infty} \binom{l+N-1}{l} x^l$$

where the binomial coefficient

$$\binom{\alpha}{l} = \frac{\alpha(\alpha-1)\cdots(\alpha-l+1)}{l!}$$

is defined for real α and therefore we write

$$Z(T, V, N) = \sum_{l=0}^{\infty} \binom{l+N-1}{l} \exp\left\{-\beta\hbar\omega\left(\frac{1}{2}N + l\right)\right\}$$

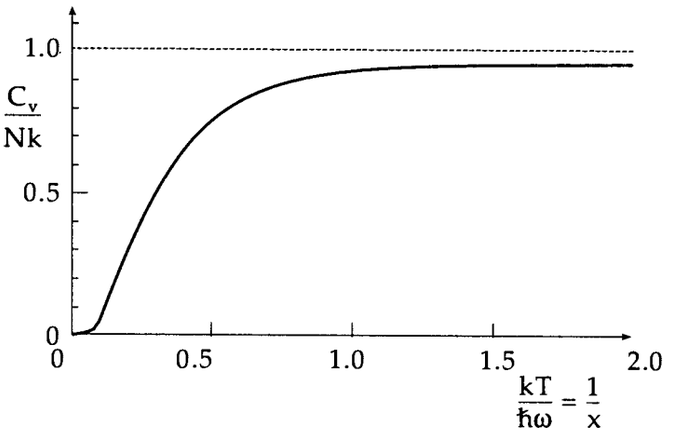


Figure 8.2. Specific heat of N quantum mechanical harmonic oscillators.

Comparing this with the general formula

$$Z(T, V, N) = \int dE g(E) \exp\{-\beta E\}$$

which for discrete enumerable energies goes over into

$$Z(T, V, N) = \sum_l g_l \exp\{-\beta E_l\}$$

(instead of the density of states now there is the degeneration factor g_l), we find

$$E_l = \hbar\omega \left(l + \frac{N}{2}\right) \qquad g_l = \binom{l + N - 1}{l} \tag{8.15}$$

The energies E_l are just the zero-point energies of the N oscillators plus l quanta of energy $\hbar\omega$. There are exactly g_l ways to distribute these *indistinguishable* energy quanta among the N *distinguishable* oscillators. One can easily see this in the following way: consider l equal balls, which have to be distributed onto N boxes, and calculate the number of different ways to do this. In doing so, recall that not only a single ball fits into one box, but that also all l balls can be put into one box, while all other boxes remain empty.

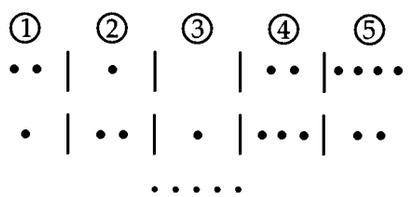


Figure 8.3. Concerning the derivation of (8.16).

Now we can put the l balls with the aid of $N - 1$ lines into N boxes (cf. Figure 8.3: left to the first line is box no. 1, etc., right to line no. $(N - 1)$ is box no. N; in the figure there are $l = 9$ (balls) and $N = 5$, i.e., four lines). We obtain all ways of subdividing the balls into boxes by drawing lines, if we consider all permutations of boxes and lines. There are exactly $(N + l - 1)!$ possibilities for the $(n - 1)$ lines plus l balls. However, the permutations of the balls among themselves do not yield a new situation, because the balls are indistinguishable. For the same reason, a permutation of the lines among themselves does not change anything in the subdivision of the balls into the N boxes. Therefore, we must divide the total number of all permutations by the numbers of the permutations of the balls, $l!$, and lines, $(N - 1)!$, leading to the result

$$g(N, l) = \frac{(N + l - 1)!}{l!(N - 1)!} = \binom{N + l - 1}{l} \tag{8.16}$$

The distribution of indistinguishable quanta instead of enumerated particles is the starting point of quantum statistics. With the degeneration factor, of course, we also know the number of microstates Ω at a given energy (8.15). It is simply $\Omega = g_l$. Thus we can check whether the entropy $S = k \ln \Omega$ coincides with expression (8.10). Using l, $N \gg 1$ and Stirling's formula for Equation (8.16), we get

$$S = k(l + N)\ln(l + N) - kl \ln l - Nk \ln N$$

To obtain $S(E, V, N), l = E/(\hbar\omega) - N/2$ must be inserted, according to Equation (8.15):

$$S = k\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right)\ln\left\{\frac{E}{\hbar\omega} + \frac{N}{2}\right\} - k\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)\ln\left\{\frac{E}{\hbar\omega} - \frac{N}{2}\right\} - Nk \ln N \tag{8.17}$$

If we want to compare this with Equation (8.10), we must express the energy in terms of the temperature,

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{k}{\hbar\omega}\ln\left\{\frac{E + \frac{N}{2}\hbar\omega}{E - \frac{N}{2}\hbar\omega}\right\}$$

or

$$E = \frac{N}{2}\hbar\omega\frac{\exp\{\beta\hbar\omega\} + 1}{\exp\{\beta\hbar\omega\} - 1} \tag{8.18}$$

which is identical to Equation (8.11). Inserting Equation (8.18) into (8.17), we indeed exactly recover Equation (8.10).

Paramagnetism

An especially interesting application of classical statistical mechanics (Boltzmann statistics, canonical ensemble) is the paramagnetic behavior of substances. It is well known that the atoms of many substances have a permanent magnetic dipole moment $\vec{\mu}$. If such a substance is subject to an external magnetic field $\vec{H}$, then the dipoles try to align in the direction of the field, so that the potential energy $-\vec{\mu} \cdot \vec{H}$ of each dipole becomes minimal (principle of least energy). In this case all magnetic moments of the atoms add up to the total magnetic moment $\vec{D}_m$ of the substance. On the other hand, at a given temperature the statistical motion of the dipoles counteracts the alignment. Namely, there are many more microstates if the magnetic moments have an arbitrary orientation compared to the case when all of them point in the same direction (principle of maximal entropy). In the limit of very high temperature, therefore, all dipoles are statistically distributed, and the magnetic moments cancel each other, so that the total moment $\vec{D}_m$ vanishes. In the case of a finite temperature and a finite magnetic field, the mean total moment $\left\langle \vec{D}_m \right\rangle$ is somewhere between these extreme cases.

As a model of a paramagnetic substance we consider a system of N freely revolvable dipoles, the translational motion of which we neglect. (In a solid the atoms are placed at certain grid positions, but also for paramagnetic fluids and gases the translational motions and the magnetic properties can be assumed to be independent of each other.)

Hence we must calculate the partition function of a system with the energy

$$E = -\sum_{i=1}^{N} \vec{\mu}_i \cdot \vec{H} \tag{8.19}$$

If the homogeneous field $\vec{H}$ points in z-direction, then the orientation of each dipole can be expressed by the polar angles θ_i and ϕ_i. Each microstate corresponds exactly to a set $\{\theta_i, \phi_i\}$ of orientations of all dipoles. The partition function over all microstates depends on T, H, and N, where the magnetic field plays a role similar to that which the volume usually plays:

$$Z(T, H, N) = \int d\Omega_1 \int d\Omega_2 \cdots \int d\Omega_N \exp\left\{\beta\mu H \sum_{i=1}^{N} \cos\theta_i\right\} \tag{8.20}$$

if $\vec{\mu}_i \cdot \vec{H} = \mu_{z_i} H_z = \mu H \cos\theta_i$ is assumed. The integrals $\int d\Omega_i$ extend over all spatial angles. The partition function factors, since we have not assumed any interaction between the individual dipoles:

$$\begin{aligned} Z(T, H, N) &= [Z(T, H, 1)]^N \\ Z(T, H, 1) &= \int d\Omega \exp\{\beta\mu H \cos\theta\} \end{aligned} \tag{8.21}$$

For the integral we obtain, with the substitution $\cos\theta = x$,

$$\begin{aligned} Z(T, H, 1) &= 2\pi \int_{-1}^{1} dx \exp\{\beta\mu H x\} \\ &= \frac{2\pi}{\beta\mu H} \left(\exp\{\beta\mu H\} - \exp\{-\beta\mu H\}\right) \\ &= 4\pi \frac{\sinh(\beta\mu H)}{\beta\mu H} \end{aligned} \tag{8.22}$$

The probability for a dipole to assume an orientation between θ, $\theta + d\theta$ and ϕ, $\phi + d\phi$ is given by

$$\rho(\theta, \phi)\, d\Omega = \frac{\exp\{\beta\mu H \cos\theta\}}{Z(T, H, 1)} \sin\theta\, d\theta\, d\phi \tag{8.23}$$

Analogously, the probability of finding dipole 1 in $d\Omega_1$, dipole 2 in $d\Omega_2$, etc., is a product of terms of the form (8.23). With the aid of Equation (8.23), the mean magnetic moment $\langle\vec{\mu}\rangle$ of a dipole can be calculated. To do this we rewrite $\vec{\mu} = \mu\vec{e}_r$ in Cartesian coordinates and find

$$\langle\vec{\mu}\rangle = \frac{1}{Z} \int \mu \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix} \exp\{\beta\mu H \cos\theta\} \sin\theta\, d\theta\, d\phi \tag{8.24}$$

We see at once that $\langle \mu_x \rangle = \langle \mu_y \rangle = 0$. The reason is that all orientations of the dipole perpendicular to the z-axis are equally probable. For $\langle \mu_z \rangle$ we obtain

$$\langle \mu_z \rangle = \frac{\mu}{Z} \int \cos\theta \exp\{\beta \mu H \cos\theta\} \sin\theta \, d\theta \, d\phi \tag{8.25}$$

Of course, this integral can be easily calculated (which is left as an exercise for the reader). We want to pursue another path. One can write

$$\langle \mu_z \rangle = \frac{1}{\beta} \frac{\partial}{\partial H} \ln Z(T, H, 1) = -\frac{\partial}{\partial H} F(T, H, 1) \tag{8.26}$$

or, for the *total mean dipole moment* in z-direction,

$$\langle D_z \rangle = -\frac{\partial}{\partial H} F(T, H, N) \tag{8.27}$$

This equation explicitly reveals that the connection between the intensive variable H and the corresponding conjugate extensive variable $\langle D_z \rangle = N \langle \mu_z \rangle$ is completely analogous to the relation between the extensive variable V and the intensive variable p in the case of an ideal gas: one obtains $\langle D_z \rangle$ or p (up to a sign) by differentiation of F with respect to H or V, respectively. Thus it is here sufficient, too, to know the free energy

$$F(T, H, N) = -kT \ln Z(T, H, N) = -NkT \ln \left\{ 4\pi \frac{\sinh(\beta \mu H)}{\beta \mu H} \right\} \tag{8.28}$$

to be able to calculate all thermodynamic quantities. Explicit calculation of Equation (8.25) or Equation (8.27), which is easier, yields

$$\langle D_z \rangle = N \langle \mu_z \rangle = N\mu \left[\coth(\beta \mu H) - \frac{1}{\beta \mu H} \right] \tag{8.29}$$

The total dipole moment as a function of the characteristic variable $x = \beta \mu H = \mu H/(kT)$ can be seen in Figure 8.4. For small x (small magnetic fields) we have

$$L(x) \approx \frac{x}{3} - \frac{x^3}{45} + \cdots \tag{8.30}$$

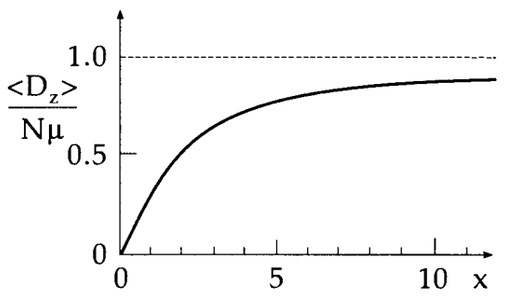


Figure 8.4. Total magnetic dipole moment, $x = \beta \mu H = \frac{\mu H}{kT}$.

where the function

$$L(x) = \coth(x) - \frac{1}{x} \tag{8.31}$$

is called the *Langevin function.*

If the magnetic field increases for finite temperature, the total dipole moment grows linearly with H. This region is interesting for nearly all temperatures. Since atomic dipole moments are of the order of magnitude of the Bohr magneton μ_B, e.g., in the case of room temperature also for very strong magnetic fields $x \ll 1$. Only in the case of very low temperatures, $T \to 0$, can the saturation region $x \gg 1$ be reached, where nearly all

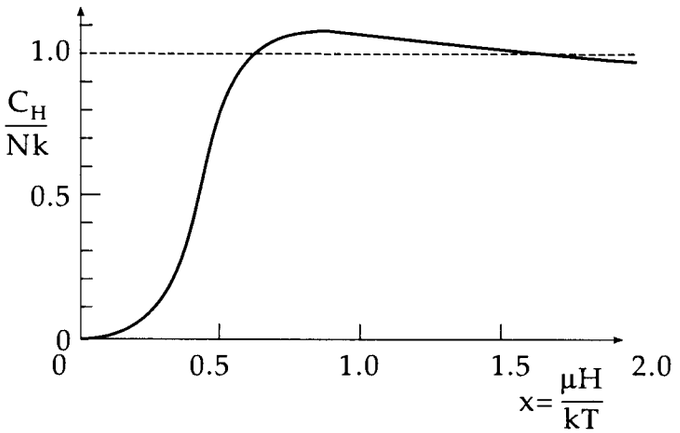


Figure 8.5. Specific heat of a paramagnet.

dipoles are aligned in field direction. There $L(x) \approx 1$. In the region $x \ll 1$ the total magnetic moment is proportional to the magnetic field,

$$\langle D_z \rangle \approx \frac{N\mu^2}{3kT} H - \cdots \tag{8.32}$$

The proportionality constant is the *susceptibility*

$$\chi = \lim_{H \to 0} \frac{\partial \langle D_z \rangle}{\partial H} = \frac{N\mu^2}{3kT} = \frac{C}{T} \tag{8.33}$$

The relation (8.33) is known as *Curie's law*. The quantity C is called *Curie's constant*. The entropy of the system results from ($x = \beta\mu H$) :

$$S(T, H, N) = -\left.\frac{\partial F}{\partial T}\right|_{H,N} = Nk \ln \left\{ 4\pi \frac{\sinh(x)}{x} \right\} - \frac{N\mu H}{T} L(x) \tag{8.34}$$

and using Equations (8.28), (8.29), and (8.34), the mean energy is given by

$$U = F + TS = -\langle D_z \rangle H \tag{8.35}$$

which is just the energy of the mean dipole in the magnetic field. This can be used, for instance, to calculate the heat capacity in the case of a constant magnetic field,

$$\begin{aligned} C_H &= \left.\frac{\partial U}{\partial T}\right|_{H,N} = \frac{\partial}{\partial x}(-N\mu L(x)) \frac{\partial x}{\partial T} \\ &= -N\mu \left[1 - \frac{x^2}{\sinh^2 x} \right] \cdot \frac{1}{x^2} \frac{\partial x}{\partial T} = \frac{Nk}{H} \left[1 - \frac{x^2}{\sinh^2 x} \right] \end{aligned} \tag{8.36}$$

This specific heat shows an interesting behavior. Since for high temperatures ($x \to 0$) we have $U \approx 0$, C_H approaches 0, too (which can be proven by expansion of the $\sinh^2 x$ in Equation (8.36)). This is typical for systems whose energy has an upper limit. Here the energy U also can never become larger than zero for $T \to \infty$ (complete statistical orientation), and the system cannot absorb further energy, $C_H(T \to \infty) = 0$.

Therefore, in the case of high temperatures the magnetic dipoles do not yield any contribution to the heat capacity of paramagnetic substances.

Up to now, we have considered classical dipoles, which can assume all possible orientations. However, the magnetic moment of atoms is caused by electrons moving around the nucleus; i.e., it is a quantum mechanical quantity. Therefore we want to perform the same considerations once again for quantum mechanical dipoles. Assume again a magnetic field H in z-direction. In quantum mechanics, $\vec{\mu}$ is an operator which is defined by

$$\hat{\vec{\mu}} = \left(g_l \hat{\vec{l}} + g_s \hat{\vec{s}}\right) \mu_B \tag{8.37}$$

Here $\hat{\vec{l}}$ is the angular momentum operator and $\hat{\vec{s}}$ is the spin operator, all of which are now dimensionless. The factor $\hbar$ has been incorporated into the Bohr magneton $\mu_B = e\hbar/(2mc)$. Equation (8.37) is motivated by the fact that the magnetic moment of an electron rotating on a sphere is classically proportional to the angular momentum of the electron.

Analogously, the magnetic moment of a rotating charged body is proportional to its spin (proper angular momentum). However, in general the constants of proportionality g_l and g_s can be different. For electrons we have, e.g., $g_l = 1$ and $g_s \approx 2$. In Volume 1 of the lectures: *Quantum Mechanics I, An Introduction* (Springer 1989) this, and especially the definition of the gyromagnetic factors (*g-factors*), have been extensively discussed.

Then $\vec{\mu}$ is no longer proportional to the total angular momentum $\vec{j} = \vec{l} + \vec{s}$, and thus it is no longer a conserved quantity. In systems with conserved total angular momentum (e.g., atoms), $\vec{\mu}$ will precess around $\vec{j}$, and in the mean only the projection of $\vec{\mu}$ onto $\vec{j}$ will remain constant,

$$\vec{\mu}_p = \frac{\vec{\mu} \cdot \vec{j}}{|\vec{j}|} \frac{\vec{j}}{|\vec{j}|} = \left(g_l \vec{l} \cdot \vec{j} + g_s \vec{s} \cdot \vec{j}\right) \mu_B \frac{\vec{j}}{|\vec{j}|^2} \tag{8.38}$$

Inserting here $\vec{j} = \vec{l} + \vec{s}$ and $\vec{l} \cdot \vec{s} = \frac{1}{2}(\vec{j}^2 - \vec{l}^2 - \vec{s}^2)$, after multiplying the factors out we obtain

$$\vec{\mu}_p = \frac{1}{2}\left((g_l - g_s)\vec{l}^2 + (g_s - g_l)\vec{s}^2 + (g_l + g_s)\vec{j}^2\right) \mu_B \frac{\vec{j}}{|\vec{j}|^2} \tag{8.39}$$

In a given electron state in the atom, now, $\vec{l}^2$, $\vec{s}^2$, and $\vec{j}^2$ are good quantum numbers, and in Equation (8.39) we can replace these quantities by their eigenvalues $l(l+1)$, $s(s+1)$, and $j(j+1)$ (without the factor $\hbar^2$, since $\hbar$ has been incorporated into μ_B from the beginning). We obtain

$$\vec{\mu}_p = g\mu_B \vec{j}$$

$$g = \left(\frac{3}{2} + \frac{s(s+1) - l(l+1)}{2j(j+1)}\right) \tag{8.40}$$

where the values $g_l = 1$ and $g_s = 2$ for electrons have been inserted. The projection factor g is the *gyromagnetic ratio* or *Lande factor*. Equation (8.40) remains valid also for the total magnetic moment of all electrons, if correspondingly the total quantities S, L, and J are inserted.

The possible energy eigenvalues of a dipole in the magnetic field are

$$E = -\vec{\mu}_p \cdot \vec{H} = -g\mu_B H j_z = -g\mu_B H m$$

$$m = -j, -j+1, \ldots, +j \tag{8.41}$$

if m is the component of $\vec{j}$ in field direction (z-direction). For a system of N dipoles we have the partition function

$$Z(T, H, N) = \sum_{m_1, m_2, \ldots, m_N = -j}^{+j} \exp\left\{\beta g \mu_B H \sum_{i=1}^{N} m_i\right\} \tag{8.42}$$

because now for all N dipoles the sum must extend over all possible orientations m_i. Here again the partition function factors, as usual, for noninteracting systems:

$$Z(T, H, N) = [Z(T, H, 1)]^N \tag{8.43}$$

with

$$Z(T, H, 1) = \sum_{m=-j}^{+j} \exp\{xm\} = \sum_{m=-j}^{+j} q^m = q^{-j} \sum_{m=0}^{2j} q^m \tag{8.44}$$

where, as an abbreviation, we have introduced the characteristic parameter $x = \beta g \mu_B H$, and $q = e^x$. The geometric series in Equation (8.44) can be summed up at once, leading to the result

$$\begin{aligned} Z(T, H, 1) &= \frac{q^{-j} - q^{j+1}}{1 - q} = \frac{\exp\{-jx\} - \exp\{(j+1)x\}}{1 - \exp\{x\}} \\ &= \frac{\exp\{(j + \frac{1}{2})x\} - \exp\{-(j + \frac{1}{2})x\}}{\exp\{\frac{x}{2}\} - \exp\{-\frac{x}{2}\}} \end{aligned} \tag{8.45}$$

Using the hyperbolic sine, Equation (8.43) can be rewritten as

$$Z(T, H, N) = \left(\frac{\sinh\{\beta g \mu_B H (j + \frac{1}{2})\}}{\sinh\{\frac{1}{2}\beta g \mu_B H\}}\right)^N \tag{8.46}$$

For the free energy this yields

$$F(T, H, N) = -kT \ln Z(T, H, N) = -NkT \ln\left\{\frac{\sinh\{\beta g \mu_B H (j + \frac{1}{2})\}}{\sinh\{\frac{1}{2}\beta g \mu_B H\}}\right\} \tag{8.47}$$

Using Equation (8.27), it is again easy to calculate the *total mean magnetic moment* $\langle D_z \rangle$,

$$\begin{aligned} \langle D_z \rangle &= -\frac{\partial}{\partial H} F(T, H, N) \\ &= N g \mu_B \left\{\left(j + \frac{1}{2}\right) \coth\left(\beta g \mu_B H \left(j + \frac{1}{2}\right)\right)\right. \\ &\quad \left. - \frac{1}{2} \coth\left(\frac{1}{2}\beta g \mu_B H\right)\right\} \end{aligned} \tag{8.48}$$

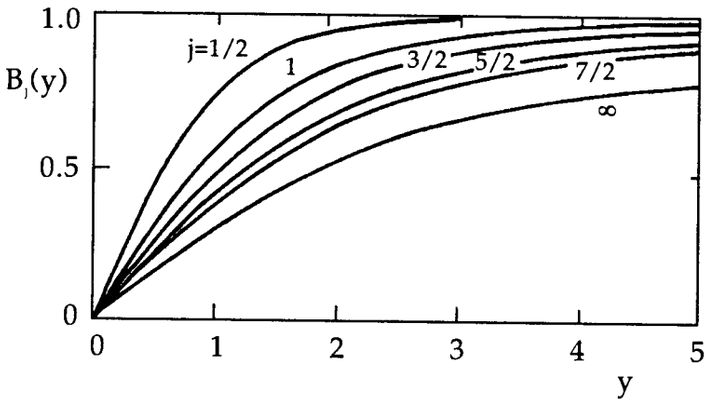


Figure 8.6. Brillouin functions.

Here one introduces, as an abbreviation in analogy to the Langevin function, the so-called *Brillouin function* with the index j,

$$B_j(y) = \left(1 + \frac{1}{2j}\right) \coth\left\{\left(1 + \frac{1}{2j}\right) y\right\} - \frac{1}{2j} \coth\left\{\frac{y}{2j}\right\} \tag{8.49}$$

Using this and considering $y = \beta g \mu_B H j$, Equation (8.48) becomes

$$\langle D_z \rangle = N g \mu_B j B_j(y) \tag{8.50}$$

The function $B_j(y)$ is depicted for different values of j in Figure 8.6. For $j \to \infty$ we obtain $B_j(y) \to L(y)$, the classical result, since a quantum mechanical dipole with $j \to \infty$ also has nearly continuously many possibilities of orientation.

Naturally, the largest deviations occur for $j = 1/2$. Dipoles with $j = 1/2$ can be more easily aligned than those with $j \to \infty$, since in the former case thermal motion cannot so easily turn the dipoles out of the field direction. Namely, the dipole can either be parallel or antiparallel to the field direction. For high temperatures, $y = \beta g \mu_B H j \to 0$, $B_j(y)$ is linear, too:

$$B_j(y) \approx \frac{1}{3}\left(1 + \frac{1}{j}\right) y - \frac{1}{45}\left\{\left(\frac{2j+1}{2j}\right)^4 - \left(\frac{1}{2j}\right)^4\right\} y^3 + \cdots \tag{8.51}$$

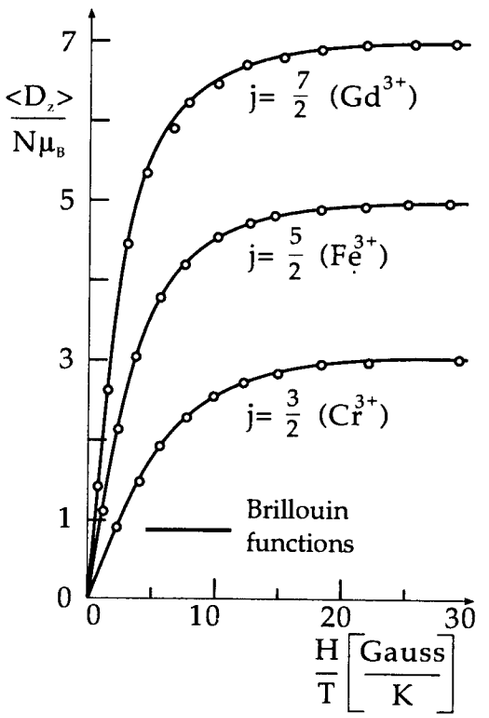


Figure 8.7. Dipole moment: calculation and experiment.

and the susceptibility follows from

$$\langle D_z \rangle \approx N \frac{g^2 \mu_B^2 j(j+1)}{3kT} H$$

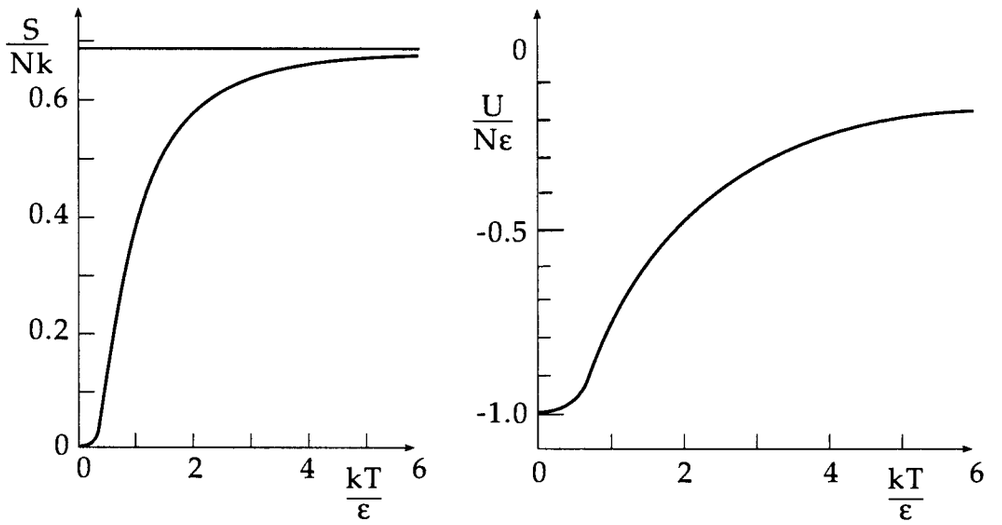


Figure 8.8. Entropy and internal energy of a system of dipoles with $|s| = \frac{1}{2}$.

$$\Rightarrow \chi = N\frac{g^2\mu_B^2 j(j+1)}{3kT} = \frac{C}{T} \tag{8.52}$$

The classical limit can also be confirmed: again the Curie law is valid, however, with a different constant C. If one inserts for the classical dipole moment μ in Equation (8.33) $\mu = g\mu_B j$, then the case $j \to \infty$ just reproduces Equation (8.52). Figure 8.7 demonstrates how well this theory agrees with experiment.

Because of its special significance, we still want to examine the case $j = 1/2$ in more detail. With $g = 2$ the dipole has then only the two possible energy values:

$$E = -g\mu_B Hm, \qquad m = -\frac{1}{2}, +\frac{1}{2},$$

$$E = \begin{cases} +\epsilon & m = -\frac{1}{2} \\ -\epsilon & m = +\frac{1}{2} \end{cases} \tag{8.53}$$

with $\epsilon = \mu_B H$. The single particle partition function is simply

$$\begin{aligned} Z(T, H, 1) &= \sum_{m=-\frac{1}{2}}^{+\frac{1}{2}} \exp\{-\beta E\} \\ &= \exp\{\beta\epsilon\} + \exp\{-\beta\epsilon\} \\ &= 2\cosh(\beta\epsilon) \end{aligned} \tag{8.54}$$

The N-particle partition function is again $Z(T, H, N) = [Z(T, H, 1)]^N$. For the free energy this means

$$F(T, H, N) = -NkT \ln\{2\cosh(\beta\epsilon)\} \tag{8.55}$$

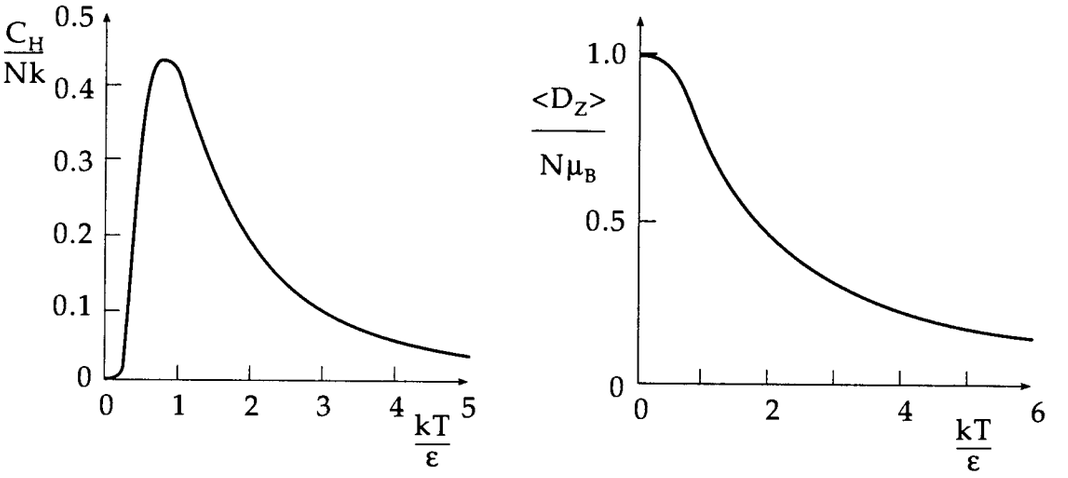


Figure 8.9. Specific heat and total magnetic moment of a system of dipoles with $|s| = \frac{1}{2}$.

This is a special case of Equations (8.45–47) for $j = 1/2$, if we take into account the addition theorems of the hyperbolic functions. Equation (8.55) yields the thermodynamic properties

$$S(T, H, N) = -\left.\frac{\partial F}{\partial T}\right|_{H,N} = Nk\,[\ln\{2\cosh(\beta\epsilon)\} - \beta\epsilon\tanh(\beta\epsilon)] \tag{8.56}$$

$$U = F + TS = -N\epsilon\tanh(\beta\epsilon) \tag{8.57}$$

$$\langle D_z \rangle = -\left.\frac{\partial F}{\partial H}\right|_{T,N} = N\mu_B\tanh(\beta\epsilon) \tag{8.58}$$

$$C_H = \left.\frac{\partial U}{\partial T}\right|_{H} = Nk(\beta\epsilon)^2\cosh^{-2}(\beta\epsilon) \tag{8.59}$$

These quantities are shown as a function of $1/\beta\epsilon = kT/\epsilon$ in Figures 8.8 and 8.9. The entropy vanishes for $T \to 0$, since here we have only a single possible state for the whole system (total alignment, $\Omega = 1$). One can also verify this directly using Equation (8.56). For $T \to \infty$ there are 2 states available for each dipole ($\uparrow$, $\downarrow$); therefore, we have $\Omega = 2^N$, and the entropy S/Nk approaches the value $\ln 2$. This can also be immediately verified by use of Equation (8.56). As one can see, entropy in quantum mechanics is a very vivid quantity.

The internal energy at $T = 0$ has exactly the value $U = -N\epsilon$, since all dipoles are aligned. From Equation (8.59) one can read that for $T = 0(x \to \infty)$ the heat capacity approaches zero like x^2e^{-2x}. This means that the system at $T = 0$ does not absorb any energy. Or, stated differently, no dipoles can be disaligned from the total alignment of all dipoles as long as $\beta\epsilon \gg 1$.

For $T \to \infty$, U approaches zero (statistical orientation of all dipoles). Here also the system cannot absorb arbitrary increments of energy (cf. Equation (8.59)).

This behavior shows a basic difference from the classical treatment of paramagnetism. In the classical case, we had $C_H \to 0$ for $T \to \infty$, since for high temperatures $U =$

const. $= 0$. This remains valid in the quantum mechanical case. However, in the case of low temperatures the classical system has a constant heat capacity $C_H \approx Nk$; i.e., the classical dipoles can also absorb small thermal energies kT. The quantum mechanical dipoles, however, can be excited by thermal energies $kT \ll \epsilon$ only with extremely low probability; i.e., $C_H \to 0$ for $T \to 0$, as derived above.

This is again an example of the fact that quantum systems with a discrete spectrum obey $C \to 0$ for $T \to 0$. The specific heat therefore shows a maximum which is located at approximately $\epsilon \approx kT$. Such a heat capacity with the general form

$$C = Nk \left(\frac{\Delta}{kT}\right)^2 \exp\left\{\frac{\Delta}{kT}\right\} \left(1 + \exp\left\{\frac{\Delta}{kT}\right\}\right)^{-2} \tag{8.60}$$

is characteristic for two-level systems with an excitation gap $\Delta = 2\epsilon$. It is known as the *Schottky heat capacity*, and its significance lies in the fact that many systems can be treated as two-level systems.

Negative temperatures in two-level systems

The example of a paramagnetic system with $j = 1/2$ (two-level system) allows us to discuss a possible extension of the notion of temperature. Each of the N particles of the system shall be able to assume two possible energies, $\pm\epsilon$. Let the number of particles in the level $+\epsilon$ be N_+, and that in $-\epsilon$ be N_-. Of course we have

$$N = N_+ + N_- \tag{8.61}$$

The total energy of the system is

$$E = (N_+ - N_-)\,\epsilon \tag{8.62}$$

Equations (8.61) and (8.62) can be solved for N_+ and N_-,

$$N_+ = \frac{1}{2}\left(N + \frac{E}{\epsilon}\right)$$

$$N_- = \frac{1}{2}\left(N - \frac{E}{\epsilon}\right) \tag{8.63}$$

The number Ω of possible states of the system at a given energy E and particle number N (microcanonical) is

$$\Omega(E, N) = \frac{N!}{N_+!N_-!} = \frac{N!}{\left[\frac{1}{2}\left(N + \frac{E}{\epsilon}\right)\right]!\left[\frac{1}{2}\left(N - \frac{E}{\epsilon}\right)\right]!} \tag{8.64}$$

Namely, there are exactly $N!$ ways to give the particles a different enumeration, where, however, different enumerations of the particles in the state $+\epsilon$ among each other ($N_+!$) yield no new situation (just like different enumerations of the particles in $-\epsilon$($N_-!$)). Equation

(8.64) immediately allows for the calculation of the entropy of the system,

$$S(E, N) = kN \ln N - k\frac{1}{2}\left(N + \frac{E}{\epsilon}\right)\ln\left\{\frac{1}{2}\left(N + \frac{E}{\epsilon}\right)\right\} - k\frac{1}{2}\left(N - \frac{E}{\epsilon}\right)\ln\left\{\frac{1}{2}\left(N - \frac{E}{\epsilon}\right)\right\} \tag{8.65}$$

where again Stirling's formula has been used for $N_+, N_- \gg 1$. Equation (8.65) yields for the temperature

$$\frac{1}{T} = \beta k = \left.\frac{\partial S}{\partial E}\right|_N = \frac{k}{2\epsilon}\ln\left\{\frac{N - \frac{E}{\epsilon}}{N + \frac{E}{\epsilon}}\right\} \tag{8.66}$$

As long as $E < 0$; i.e., there are more particles in the lower level $-\epsilon$, we have $T > 0$, as usual. If temperature is taken as the variable, then for $T \to \infty$ the particles distribute themselves equally on the upper and the lower levels ($N_+ = N_- \Rightarrow E = 0$).

Thus this does not lead to a new situation. However, the particles of such a system can be excited by special mechanisms, so that an over-occupation of the higher level $+\epsilon$ is reached. In lasers this mechanism is called pumping; for instance, it can be done optically using light radiation. The precondition in this case is, however, that the particles remain in the upper level (metastable level) for a sufficiently long time; otherwise a high occupation in $N_+ \gg N_-$ cannot be achieved. A state with $N_+ \gg N_-$ is also called *inversion*. Because $E = (N_+ - N_-)\epsilon > 0$, to an inverted state there corresponds a negative temperature according to Equation (8.66)!

To understand this a little better, we plot $S/(Nk)$ according to Equation (8.65) as a function of $E/(N\epsilon)$ (Figure 8.10). For $E/(N\epsilon) = -1$ all particles are in the lower level. The slope $\beta \propto \partial S/\partial E$ is infinite, and $T = 0$.

In the case of equal distribution in the upper and the lower levels ($N_+ = N_-$), we have $E/(N\epsilon) = 0$ and the slope $\beta = 0$. Here the temperature suddenly jumps from $+\infty$ to $-\infty$, as soon as there are slightly more particles in the upper level. If finally all particles are collected in the upper level (pumping!), we have $E/(N\epsilon) = 1$, and again $T = 0$.

Thus, in such a system it is indeed reasonable to describe an inverted state by a negative temperature. Such inverted states are significant not only in lasers; substances with a nuclear magnetic moment also can be inverted. To do this, one only has to align as many dipoles as possible by a high magnetic field at not too high temperatures.

If now the field direction is suddenly reversed, nearly all the particles are in the "wrong" state (inversion). Of course, they will go over into a more convenient state with a certain relaxation time, but during this time one can attach to them a negative temperature.

In practice, this situation can be reached in lithium fluoride (Purcell and Pound 1951). The nuclear spins are aligned by a strong magnetic field. Thermal equilibrium of the spins among each other is reached after a relaxation time τ_1, which has the order of magnitude of 10^{-5} s. If now the field is suddenly reversed, one has an inverted state, in which the spins after 10^{-5} s are indeed in equilibrium among each other. It is therefore reasonable to attach to this state a negative temperature of the spins. One must be aware of the fact that the whole LiF crystal is still at laboratory temperature—only the spin system is influenced

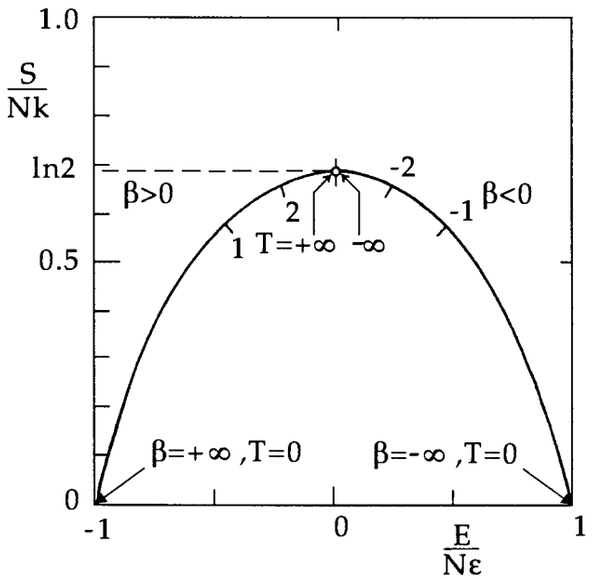


Figure 8.10. Concerning the problem of negative temperatures.

by the field inversion. Now the relaxation time necessary to obtain thermal equilibrium between the spins and the crystal grid is very large, $\tau_2 \approx 5$ min. Therefore, during this time τ_2 one can determine the negative temperature of the spin system by the negative nuclear magnetic moment. Not until about 5 minutes later is the system again in equilibrium at laboratory temperature.

Finally, we remark that only for systems having an upper limit for the energy can negative temperatures reasonably be defined. Only then does the curve $S(E)$ behave as shown in Figure 8.10, with a region $\beta \propto \partial S/\partial E < 0$. If the energy is able to increase to infinity, then in general the entropy (number of states) always increases further.

Gases with internal degrees of freedom

In our treatment of the ideal gas we have assumed the particles to be ideal mass points. However, this is a reasonable approximation only for monatomic noble gases. In contrast, most gases consist of molecules which can perform internal motion (rotations, vibrations, etc.). We now want to calculate their influence on the thermodynamic properties.

In many cases, it is a good approximation to assume that the single degrees of freedom of a molecule are independent of each other. Let the Hamiltonian of a single molecule be of the form

$$H = H_{\text{trans}}(\vec{R}, \vec{P}) + H_{\text{rot}}(\phi_i, p_{\phi_i}) + H_{\text{vib}}(q_j, p_j) \tag{8.67}$$

The first term H_{trans} describes the translation of the center of mass $\vec{R}$ of the molecule, the second term H_{rot} is the rotational energy, which depends on the Euler angles $\phi_i = (\theta, \phi, \psi)$ and the corresponding angular momenta. Finally, H_{vib} is the energy of the vibrations of the molecule, which are described by the generalized coordinates of the normal vibrations q_j

and the corresponding momenta. In Equation (8.67), the interactions between the degrees of freedom ($H_{\text{rot vib}}$), which come for example from the change of the moment of inertia due to the vibrations, are neglected. The advantage of Equation (8.67) is that the single-particle partition function factors just as in the case of noninteracting particles:

$$\begin{aligned} Z(T, V, 1) &= \frac{1}{h^3}\int d^3R \int d^3P \frac{1}{h^3}\int d^3\phi \int d^3p_\phi \frac{1}{h^f}\int d^f q \\ &\quad \times \int d^f p \exp\{-\beta (H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}})\} \\ &= Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} \end{aligned} \tag{8.68}$$

with

$$Z_{\text{trans}} = \frac{1}{h^3}\int d^3R \int d^3P \exp\{-\beta H_{\text{trans}}\} \tag{8.69}$$

$$Z_{\text{rot}} = \frac{1}{h^3}\int d^3\phi \int d^3p_\phi \exp\{-\beta H_{\text{rot}}\} \tag{8.70}$$

$$Z_{\text{vib}} = \frac{1}{h^f}\int d^f q \int d^f p \exp\{-\beta H_{\text{vib}}\} \tag{8.71}$$

The total partition function of a gas with N molecules results as

$$Z(T, V, N) = \frac{1}{N!}[Z(T, V, 1)]^N = \frac{1}{N!} Z_{\text{trans}}^N Z_{\text{rot}}^N Z_{\text{vib}}^N \tag{8.72}$$

The free energy of the gas for $N \gg 1$ becomes

$$\begin{aligned} F(T, V, N) &= -kT \ln Z(T, V, N) \\ &= -NkT\left[\ln\left\{\frac{Z_{\text{trans}}}{N}\right\} + 1\right] - NkT \ln Z_{\text{rot}} - NkT \ln Z_{\text{vib}} \\ &= F_{\text{trans}} + F_{\text{rot}} + F_{\text{vib}} \end{aligned} \tag{8.73}$$

Note: the free energy of the translation is $F(T, V, N) = -kT \ln Z_{\text{trans}}(T, V, N) = -kT \ln \frac{1}{N!} Z_{\text{trans}}(T, V, 1)^N = -NkT[\ln\{\frac{Z_{\text{trans}}(T,V,1)}{N}\} + 1]$. The total free energy is simply the sum of the contributions to the single degrees of freedom. The same is valid of course for all other extensive quantities of state. Using

$$H_{\text{trans}} = \frac{\vec{P}^2}{2M} \tag{8.74}$$

the translation leads to the partition function of the ideal gas,

$$Z_{\text{trans}} = V\left(\frac{2\pi MkT}{h^2}\right)^{3/2} \tag{8.75}$$

Therefore the part F_{trans} is identical to the free energy of an ideal gas. The Lagrangian of a symmetric rotor with the moments of inertia I_1, I_2, and I_3 expressed by the Euler angles θ,

ϕ, and ψ, is, according to Figure 8.11,

$$L_{\text{rot}} = \frac{I_1}{2}(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta) + \frac{I_3}{2}(\dot{\psi} + \dot{\phi}\cos\theta)^2 \tag{8.76}$$

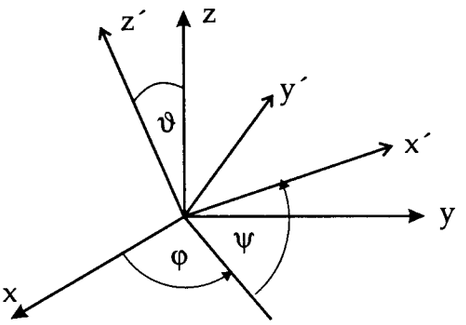


Figure 8.11. Euler angles.

If we express the time derivatives of the Euler angles by the corresponding canonical momenta, $p_{\phi_i} = \frac{\partial L}{\partial \dot{\phi}_i}$, then the Hamiltonian is

$$H_{\text{rot}} = \frac{p_\theta^2}{2I_1} + \frac{p_\psi^2}{2I_3} + \frac{(p_\phi - p_\psi\cos\theta)^2}{2I_1\sin^2\theta} \tag{8.77}$$

The angles θ, ϕ, and ψ are in the ranges $\theta \in [0, \pi]$, $\phi \in [0, 2\pi]$, and $\psi \in [0, 2\pi]$. Here the angle ψ describes the rotation around the symmetry axis z' of the gyroscope (cf. Volume 2 of this series). For the partition function Z_{rot} this yields

$$Z_{\text{rot}} = \frac{1}{h^3}\int d\theta\, d\phi\, d\psi \int_{-\infty}^{+\infty} dp_\theta\, dp_\phi\, dp_\psi \exp\left\{-\beta\left(\frac{p_\theta^2}{2I_1} + \frac{p_\psi^2}{2I_3} + \frac{(p_\phi - p_\psi\cos\theta)^2}{2I_1\sin^2\theta}\right)\right\} \tag{8.78}$$

At first glance, these integrals look a little deterrent, but they are easy to solve. First, the integrand does not depend on ϕ and ψ, so that these integrals simply contribute a factor $(2\pi)^2$. The integral over p_θ is a Gaussian integral with the value $\sqrt{2\pi I_1/\beta}$, and we are left with

$$Z_{\text{rot}} = \frac{(2\pi)^2}{h^3}\sqrt{\frac{2\pi I_1}{\beta}}\int_0^\pi d\theta \int_{-\infty}^{+\infty} dp_\psi \exp\left\{-\beta\frac{p_\psi^2}{2I_3}\right\} \times \int_{-\infty}^{+\infty} dp_\phi \exp\left\{-\beta\frac{(p_\phi - p_\psi\cos\theta)^2}{2I_1\sin^2\theta}\right\} \tag{8.79}$$

The last integral is again a Gaussian integral, but with a shifted origin. However, it is well known that the value of a Gaussian integral does not depend on the position of the origin, and we obtain

$$Z_{\text{rot}} = \frac{(2\pi)^2}{h^3}\sqrt{\frac{2\pi I_1}{\beta}}\int_0^\pi d\theta \int_{-\infty}^{+\infty} dp_\psi \exp\left\{-\beta\frac{p_\psi^2}{2I_3}\right\}\sqrt{\frac{2\pi I_1}{\beta}}\sin\theta \tag{8.80}$$

The last two integrals factor and yield, with the use of $\hbar = h/2\pi$:

$$Z_{\text{rot}} = \frac{1}{\pi\hbar^3}\sqrt{\frac{2\pi I_1}{\beta}}\sqrt{\frac{2\pi I_1}{\beta}}\sqrt{\frac{2\pi I_3}{\beta}} \tag{8.81}$$

The partition function has quite an analogous form to that of the translation; however, now we must replace $V^{1/3}\sqrt{2\pi MkT/h^2}$ by $\pi^{-1/3}\sqrt{2\pi IkT/\hbar^2}$. Observe, that Equation (8.81) is dimensionless, too, since the moment of inertia has the dimension [mass] · [length]^2.

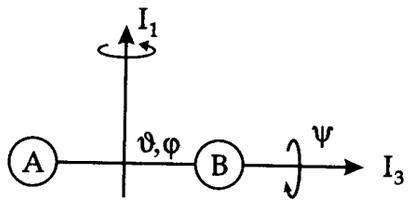


Figure 8.12. Two-atom molecule.

A particularly interesting special case is that of two-atom molecules like HCl, H_2, O_2, N_2, etc. (See Figure 8.12.) For these, the moment of inertia I_3 around the symmetry axis is very small. However, now one may not simply set $I_3 = 0$ in Equation (8.81), since in that case Z_{rot} would vanish identically. The reason for this is that in the transition from Equation (8.76) to (8.77) we divided by I_3. Therefore, we must eliminate the degree of freedom ψ in the Lagrangian. This leads to

$$H'_{\text{rot}} = \frac{p_\theta^2}{2I_1} + \frac{p_\phi^2}{2I_1 \sin^2\theta} \tag{8.82}$$

Therefore, the calculation must be performed again from the beginning. We find that the last square root in Equation (8.81), which belongs to the rotation ψ, simply drops out:

$$Z'_{\text{rot}} = \frac{2I_1 kT}{\hbar^2} \tag{8.83}$$

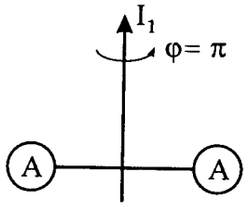


Figure 8.13. Homonuclear molecule.

For two-atom molecules consisting of identical atoms another peculiarity has to be taken into account. If such a molecule (N_2, O_2, etc.) is rotated about $\phi = \pi$, the initial situation is recovered, since both atoms are indistinguishable. This means that in this case the angle ϕ does not run from 0 to 2π, but only from 0 to π, since all angles $\phi > \pi$ lead to a microstate which has already been taken into account. Since the integral $\int d\phi$ contributes only a factor 2π, in Equation (8.83) for homonuclear molecules the factor 2 drops out. This is a problem which is completely analogous to the Gibbs' factor, and which cannot be understood classically.

Hence, the free energy of the rotations for two-atom molecules is

$$F'_{\text{rot}} = -NkT \ln Z'_{\text{rot}} = -NkT \ln \left\{ \frac{\phi_{\max} I_1 kT}{\pi\hbar^2} \right\} \tag{8.84}$$

where in general $\phi_{\max} = 2\pi$, and where in the homonuclear case $\phi_{\max} = \pi$. The entropy becomes

$$S'_{\text{rot}} = -\left.\frac{\partial F'_{\text{rot}}}{\partial T}\right|_N = Nk\left[\ln\left\{\frac{\phi_{\max} I_1 kT}{\pi\hbar^2}\right\} + 1\right] \tag{8.85}$$

and the contribution to the internal energy is

$$U'_{\text{rot}} = F'_{\text{rot}} + TS'_{\text{rot}} = NkT \tag{8.86}$$

Correspondingly, for gases with several atoms the full partition function (8.81) must be inserted,

$$F_{\text{rot}} = -NkT \ln Z_{\text{rot}} = -NkT \ln \left\{ \frac{1}{\pi}\sqrt{\frac{2\pi I_1}{\hbar^2}}\sqrt{\frac{2\pi I_1}{\hbar^2}}\sqrt{\frac{2\pi I_3}{\hbar^2}}(kT)^{3/2} \right\} \tag{8.87}$$

TABLE 8.1 Specific heats of gases at T = 20°C extrapolated to low pressure (p → 0)

Gas	Number of degrees of freedom			C_V^{exp}[J K^{-1}mol^{-1}]	C_V^{theo}[J K^{-1}mol^{-1}]
	trans	rot	total		
He	3	0	3	12.6	12.47
Ar	3	0	3	12.4	12.47
O_2	3	2	5	21.0	20.78
N_2	3	2	5	20.7	20.78
H_2	3	2	5	20.2	20.78
NH_3	3	3	6	25.1	27.35
H_2O_{vap}	3	3	6	26.5	25.81

$$S_{\text{rot}} = -\frac{\partial F_{\text{rot}}}{\partial T} = Nk\left[\ln\left\{\frac{1}{\pi}\sqrt{\frac{2\pi I_1}{\hbar^2}}\sqrt{\frac{2\pi I_1}{\hbar^2}}\sqrt{\frac{2\pi I_3}{\hbar^2}}(kT)^{3/2}\right\} + \frac{3}{2}\right] \tag{8.88}$$

$$U_{\text{rot}} = F_{\text{rot}} + TS_{\text{rot}} = \frac{3}{2}NkT \tag{8.89}$$

The total internal energy results from that of the ideal gas $U_{\text{ideal}} = \frac{3}{2}NkT$ plus that of the rotations (8.86) or (8.89). For two-atom gases one obtains

$$U' = \frac{3}{2}NkT + NkT = \frac{5}{2}NkT \qquad \text{and} \qquad C'_V = \frac{5}{2}Nk \tag{8.90}$$

and for gases with more atoms

$$U = \frac{3}{2}NkT + \frac{3}{2}NkT = 3NkT \qquad \text{and} \qquad C_V = 3Nk \tag{8.91}$$

With the use of the gas constant $R = N_A k = 8.31439$ J/(K mol), one can calculate Equations (8.90) and (8.91) using the molar specific heats. A comparison of the theoretical values with the experimentally observed data is listed in Table 8.1. We have also written down the number of degrees of freedom of the molecules. The validity of the equipartition theorem is very well confirmed. The latter attaches to each degree of freedom the quantity $\frac{1}{2}kT$ as the contribution to the total internal energy per particle, and correspondingly, the quantity $\frac{1}{2}k$ as the contribution to the specific heat.

In all cases, the previously derived relation $C_p = C_V + R$ for the molar specific heats remains valid.

Now we want to examine what changes in our results if the rotation of the molecule is not treated classically, but quantum mechanically. Since the quantum mechanical theory of gyroscopes in the general case is very complicated, we restrict ourselves to a simple linear rigid rotor with two degrees of freedom for the axes of rotation and the principal moments of inertia $(I, I, 0)$. The Hamiltonian of such a gyroscope is

$$\hat{H}_{\text{rot}} = \frac{\hat{\vec{L}}^2}{2I} \tag{8.92}$$

This will yield the essential qualitative changes compared to the classical case. The eigenvalues of $\hat{H}_{\text{rot}}$ are identical to those of the angular momentum operator,

$$\epsilon_{l,m} = \frac{l(l+1)\hbar^2}{2I}, \qquad l = 0, 1, 2, \ldots, \quad m = -l, -l+1, \ldots, +l \tag{8.93}$$

The energies $\epsilon_{l,m}$ are degenerate with respect to the projection m, since for a spherical gyroscope the orientation of the rotation axis is of no importance. The partition function is:

$$Z_{\text{rot}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \exp\{-\beta\epsilon_{l,m}\} = \sum_{l=0}^{\infty}(2l+1)\exp\left\{-\beta\frac{l(l+1)\hbar^2}{2I}\right\} \tag{8.94}$$

Equation (8.94) cannot be calculated in closed form, but for high temperatures ($T \to \infty$), as well as for low temperatures ($T \to 0$), one can give good approximations. A systematic expansion of Equation (8.94) for large T is possible with the use of the Euler–MacLaurin formula, which serves to calculate the integrals numerically. The Euler–MacLaurin sum formula is:

$$\int_a^b f(x)\mathrm{d}x = h\left(\frac{1}{2}f(x_0) + \sum_{\nu=1}^{N-1} f(x_\nu) + \frac{1}{2}f(x_N)\right) + \sum_{j=1}^{N-1}\frac{B_{2j}}{(2j)!}h^{2j}\left(f^{(2j-1)}(x_0) - f^{2j-1)}(x_N)\right) + R \tag{8.95}$$

where $x_0 = a, x_N = b, h = \frac{b-a}{N}, x_j = a + jh$. The B_{2j} are the Bernoulli numbers. Now we apply this equation to the function

$$f(x) = (2x+1)e^{-\frac{\Theta}{T}x(x+1)}$$

where $\Theta = \hbar^2/2Ik$. Using $a = 0, b = 0, h = 1$ we obtain

$$\int_0^\infty f(x)\mathrm{d}x = \frac{1}{2}f(0) + \sum_{l=0}^{\infty} f(l) + \sum_{j=1}^{\infty}\frac{B_{2j}}{(2j)!}f^{(2j-1)}(0)$$

or

$$\sum_{l=0}^{\infty} f(l) = \int_0^\infty f(x)\mathrm{d}x + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) - + \cdots \tag{8.96}$$

The first term in Equation (8.95) becomes

$$\int_0^\infty f(x)\,dx = \int_0^\infty (2x+1)\exp\left\{-\frac{\Theta}{T}x(x+1)\right\}dx = \int_0^\infty \exp\left\{-\frac{\Theta}{T}y\right\}dy = \frac{T}{\Theta} \tag{8.97}$$

where we have substituted $x(x+1) = y$. The next terms are

$$f(0) = 1 \tag{8.98}$$

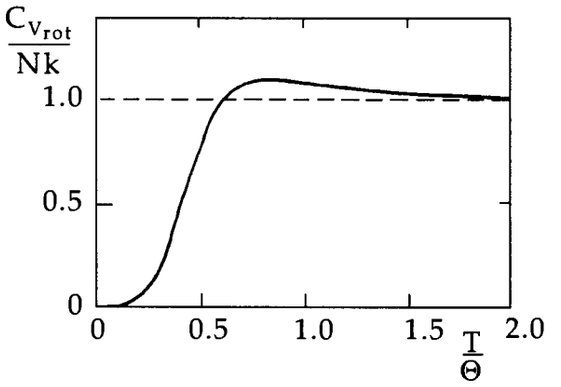


Figure 8.14. Specific heat of rotations.

$$f'(0) = 2 - \frac{\Theta}{T} \tag{8.99}$$

$$f'''(0) = -12\frac{\Theta}{T} + 12\left(\frac{\Theta}{T}\right)^2 - \left(\frac{\Theta}{T}\right)^3 \tag{8.100}$$

$$f^{(5)}(0) = 120\left(\frac{\Theta}{T}\right)^2 - 180\left(\frac{\Theta}{T}\right)^3 + 30\left(\frac{\Theta}{T}\right)^4 - \left(\frac{\Theta}{T}\right)^5 \tag{8.101}$$

Inserting this into Equation (8.95) and sorting for powers of Θ/T yields

$$Z_{\text{rot}} \approx \frac{T}{\Theta} + \frac{1}{3} + \frac{1}{15}\frac{\Theta}{T} + \frac{4}{315}\left(\frac{\Theta}{T}\right)^2 + \cdots \tag{8.102}$$

One obtains an expansion in Θ/T which is a good approximation for high temperatures. For $T \to \infty$ one obtains the classical partition function of two-atom gases (symmetric gyroscope), cf. Equation (8.83),

$$Z_{\text{rot}}(T \to \infty) \approx \frac{T}{\Theta} = \frac{2I_1 kT}{\hbar^2} \tag{8.103}$$

In this case, the mean thermal energy kT is so large that the gyroscope assumes a very high angular momentum quantum number l, and the spacing of the discrete energy levels is very small compared to kT. The other limiting case $T \to 0$ can also be easily studied. Then the summands in Equation (8.94) become very small, and it is sufficient to consider only the first summands:

$$Z_{\text{rot}}(T \to 0) \approx 1 + 3\exp\left\{-2\frac{\Theta}{T}\right\} + 5\exp\left\{-6\frac{\Theta}{T}\right\} + \cdots \tag{8.104}$$

Just as in the classical case, the free energy and all other thermodynamic properties can be calculated from the partition function Z_{rot}. In Figure 8.14 we have depicted the specific heat of the rotations (which has been calculated numerically from Equation (8.94)). For $T/\Theta \gg 1$ it approaches the classical limit, while for $T/\Theta \approx 1/2$ a steep descent sets in.

For $T/\Theta \ll 1$, Equation (8.104) yields

$$C_{V\,\mathrm{rot}} \approx 12k \left(\frac{\Theta}{T}\right)^2 \exp\left\{-2\frac{\Theta}{T}\right\} \tag{8.105}$$

i.e., an exponential decrease.

We know already a similar behavior from another quantum system (harmonic oscillators). It is typical for systems having a discrete energy spectrum. In the limit of low temperatures the mean thermal energy kT is no longer sufficient to excite the quantum mechanical gyroscopes into higher energy levels, causing the exponential decrease of the specific heat.

Before we compare this statement with experiment, we also want to calculate the contribution of the vibrations of the molecules. It is not difficult to do this at once quantum mechanically, because each of the normal vibrations of a molecule has exactly the same Hamiltonian as a harmonic oscillator:

$$\hat{H}_{\mathrm{vib}} = \sum_{i=1}^{f} \left(\frac{p_i^2}{2B_i} + \frac{1}{2} B_i \omega_i^2 q_i^2\right) \tag{8.106}$$

Here the q_i are the generalized coordinates of the normal vibrations (elongation from the rest position) and the B_i are the corresponding masses, which can be calculated from the geometry of the molecule and the masses of the involved atoms (cf. Volume 2 of this series). The proper frequencies ω_i of the normal vibrations additionally depend on the oscillator constant of the bonds in the molecule. Here we do not want to calculate these details for special molecules, because the qualitative behavior of the specific heat can also be understood without it.

According to Example 8.1, the partition function of a quantum mechanical oscillator of frequency ω is given by

$$Z_{\mathrm{osc}} = \left[2 \sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right]^{-1} \tag{8.107}$$

For the normal vibrations the total partition function results as

$$Z_{\mathrm{vib}} = \prod_{i=1}^{f} \left[2 \sinh\left(\frac{1}{2}\beta\hbar\omega_i\right)\right]^{-1} \tag{8.108}$$

The contribution to the free energy is

$$F_{\mathrm{vib}} = \sum_{i=1}^{f} kT \ln\left\{2 \sinh\left(\frac{1}{2}\beta\hbar\omega_i\right)\right\} \tag{8.109}$$

Corresponding to Equation (8.11), the internal energy is

$$U_{\mathrm{vib}} = \sum_{i=1}^{f} \hbar\omega_i \left[\frac{1}{2} + \frac{1}{\exp\{\beta\hbar\omega_i\} - 1}\right] \tag{8.110}$$

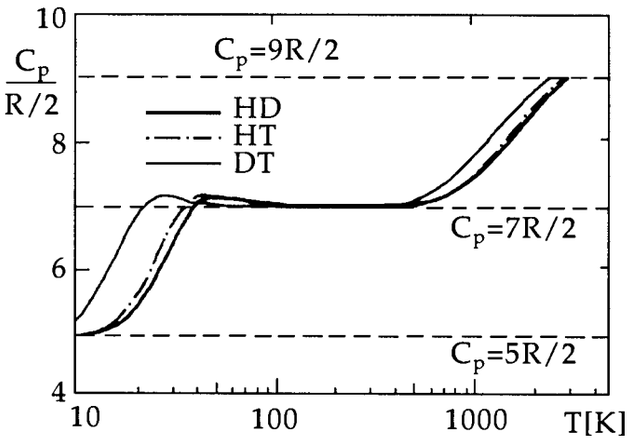


Figure 8.15. Specific heat C_p of different isotopes in the hydrogen molecule.

and the specific heat (cf. Equation (8.14)) is

$$C_{V\,\mathrm{vib}} = \sum_{i=1}^{f} k(\beta\hbar\omega_i)^2 \frac{\exp\{\beta\hbar\omega_i\}}{(\exp\{\beta\hbar\omega_i\} - 1)^2} \tag{8.111}$$

Especially for two-atom molecules there is only one normal vibration, $f = 1$, in which the atoms move exactly in opposite directions along the molecular axis. The specific heat has then exactly the behavior shown in Figure 8.2.

In general, however, the typical energies of the molecular vibrations $\hbar\omega$ are of the order of magnitude of some tenths of electron volts. This corresponds to temperatures of some thousand K. The molecular vibrations cannot show up below these temperatures.

In contrast to this, the typical energies of the rotations $\hbar^2/2I$ are of the order of magnitude of some hundredths of electron volts. At room temperature $kT \approx 1/40$ eV therefore only the rotations are of importance, in good agreement with experiment. For a two-atom gas, therefore, the following qualitative course of the molar specific heat results (here in the case of constant pressure $C_p = C_V + R$):

For very small temperatures $T \approx 10$ K only the translational motion is of importance; in the case of room temperature rotations can be excited, while for very large temperatures the vibrations also come into play. However, only a small number of gases do not become liquid at sufficiently low temperature, and so permit our theory to be checked by experiment. Such cases are, for instance, H_2 and especially the molecules HD, HT, and DT, in which a hydrogen atom is replaced by the isotopes deuterium or tritium.

One can see in Figure 8.15 that not only does the qualitative behavior agree with the prediction from the theory, but also the influence of the different moments of inertia of the molecules and the different vibration frequencies ω_i of the otherwise chemically equivalent molecules is confirmed. So DT has the largest moment of inertia I, which leads to the lowest excitation energies for rotations.

The larger mass of the isotopes D and T analogously leads to a lower frequency of the normal vibration ω compared to HT and HD. Observe that chemically (i.e., with respect

to electron configuration), the gases H_2, HD, HT, and DT are completely identical. For very large temperatures $T \approx 5000$ K the excitation of the electrons sets in, leading to a dissociation of the molecules, i.e., to ionization, so that C_p cannot be further observed experimentally.

Relativistic ideal gas

Now we turn to another system which is frequently used in particle physics: In large accelerators, as for example at the Gesellschaft für Schwerionenforschung (GSI) between Frankfurt and Darmstadt and at CERN in Geneva, it is today possible to accelerate heavy ions to very high kinetic energies $E \gg m$, and to perform experiments with them. If such particles hit a target, there are collisions between the atomic nuclei in which the nucleons are slowed down, assuming a statistically distributed kinetic energy from the former relative motion. This energy can be so large that the binding energy of the nucleons in the nucleus (some MeV) is comparatively small. Then, for short times, one obtains a gas of nucleons which in crude approximation corresponds to an ideal gas of noninteracting classical particles. The Hamiltonian of such a gas is

$$H = \sum_{i=1}^{N} mc^2 \left\{ \left[1 + \left(\frac{\vec{p}_i^{\,2}}{mc} \right)^2 \right]^{1/2} - 1 \right\} \tag{8.112}$$

Here the rest mass mc^2 of the particles has been subtracted, so that there remains only the kinetic energy. The total partition function corresponding to Equation (8.112) factors, as in general it must for noninteracting systems,

$$Z(T, V, N) = \frac{1}{N!} [Z(T, V, 1)]^N \tag{8.113}$$

with

$$Z(T, V, 1) = \frac{1}{h^3} \int d^3q \int d^3p \exp\left\{ -\beta mc^2 \left(\left[1 + \left(\frac{\vec{p}^{\,2}}{2m} \right)^2 \right]^{1/2} - 1 \right) \right\} \tag{8.114}$$

The integral over the coordinates simply yields the volume of the gas. Additionally, the integral over the momenta can be simplified by substitution of spherical polar coordinates,

$$Z(T, V, 1) = \frac{4\pi V}{h^3} \exp\{\beta mc^2\} \int_0^\infty p^2 \, dp \exp\left\{ -\beta mc^2 \left[1 + \frac{p^2}{2m} \right]^{1/2} \right\} \tag{8.115}$$

Now we perform a substitution which is useful in many relativistic problems

$$\frac{p}{mc} = \sinh x$$

$$dp = mc \cosh x \, dx$$

$$\left[1 + \left(\frac{p}{mc}\right)^2\right]^{1/2} = \cosh x \tag{8.116}$$

Then the following expression remains to be calculated,

$$Z(T, V, 1) = \frac{4\pi V}{h^3}(mc)^3 e^u \int_0^\infty dx \cosh x \sinh^2 x \exp\{-u \cosh x\} \tag{8.117}$$

where as an abbreviation the characteristic parameter $u = \beta mc^2$ has been introduced. The quantity u measures the ratio of the rest energy mc^2 of the particles to their mean thermal energy kT. The integral (8.117) can be looked up in a table. There (e.g., Gradstein–Ryshik, Volume 1, p. 409) one finds the following standard integral:

$$\int_0^\infty \exp\{-u \cosh x\} \sinh(\gamma x) \sinh x \, dx = \frac{\gamma}{u} K_\gamma(u) \tag{8.118}$$

where $K_\gamma(u)$ is one of the frequently used *cylinder functions*, which are also called the modified *Bessel functions*. In general, cylinder functions are defined as solutions of the differential equation

$$z^2 \frac{d^2w}{dz^2} + z\frac{dw}{dz} - (z^2 + \gamma^2) w = 0 \tag{8.119}$$

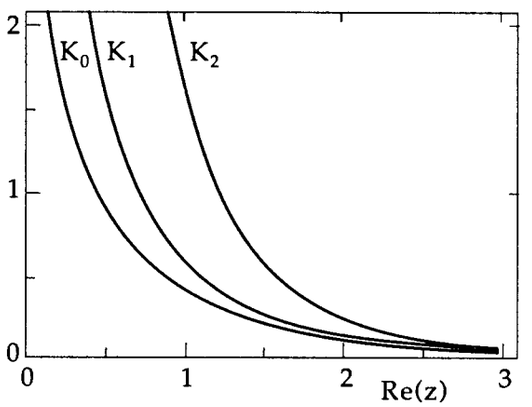


Figure 8.16. The K-functions.

where z also may be complex. The solution of Equation (8.119) which remains finite for $z = 0$ is the Bessel function $J_\gamma(z)$, while the singular solution is the *Neumann function* $N_\gamma(z)$. Of great use are the linear combinations $H_\gamma^{(1),(2)}(z) = J_\gamma(z) \pm iN_\gamma(z)$, which are called *Hankel functions of first* or *second kind*, respectively. Now, the functions $K_\gamma(z)$ are essentially Hankel functions with an imaginary argument,

$$K_\gamma(z) = \frac{\pi i}{2} \exp\left\{\frac{\pi}{2}\gamma i\right\} H_\gamma^{(1)}(iz). \tag{8.120}$$

The essential behavior of the K-functions can be seen in Figure 8.16. They are exponentially decreasing functions which diverge at $z \to 0$. The asymptotic form for small arguments ($z \ll 1$, real) and large arguments ($z \gg 1$, real) can be looked up in a formula table.

The series expansion of $K_n(z)$ is

$$\begin{aligned} K_n(z) = {} & \frac{1}{2}\sum_{k=0}^{n-1}(-)^k \frac{(n-k-1)!}{k!}\left(\frac{z}{2}\right)^{2k-n} \\ & + (-)^{n+1}\sum_{k=0}^{\infty}\frac{1}{k!(n+k)!}\left(\frac{z}{2}\right)^{2k+n} \\ & \times \left[\ln\frac{z}{2} - \frac{1}{2}\Psi(k+1) - \frac{1}{2}\Psi(n+k+1)\right] \end{aligned} \tag{8.121}$$

Here the function Ψ is the well-known Gauss function, which is the logarithmic derivative of the Γ-function: $\Psi(x) = \frac{d}{dx} \ln \Gamma(x)$. For small arguments the K-functions diverge like $K_n(z) \approx \frac{1}{2}(n-1)!(\frac{z}{2})^{-n}$, which can be seen in the series expansion (8.121). For large arguments these functions behave like modified exponential functions $\propto e^{-z}$:

$$K_n(z) = \sqrt{\frac{\pi}{2z}} e^{-z} \left\{ \sum_{k=0}^{l-1} \frac{\Gamma\left(n+k+\frac{1}{2}\right)}{k!\Gamma\left(n-k+\frac{1}{2}\right)} (2z)^{-k} + \Theta \frac{\Gamma\left(n+l+\frac{1}{2}\right)}{n!\Gamma\left(n-l+\frac{1}{2}\right)} (2z)^{-l} \right\} \tag{8.122}$$

Here l is a natural number at which the series is cut off, and $\Theta \in [0, 1]$. The last term exactly corresponds to the estimate of the error in the Taylor expansion. With the identity $\cosh x \sinh x = \frac{1}{2} \sinh(2x)$, we find for the partition function (8.117)

$$Z(T, V, 1) = \frac{4\pi V}{h^3} (mc)^3 e^u \frac{K_2(u)}{u} \tag{8.123}$$

This immediately leads to the nonrelativistic limit with $u = \beta mc^2 \to \infty$, i.e. $mc^2 \gg kT$. If the mean thermal energy kT is very small compared to the rest mass mc^2 of the particles, according to Equation (8.122) we have $K_2(u) \approx \sqrt{\pi/2u}e^{-u}$, and thus

$$Z(T, V, 1) \approx \frac{4\pi V}{h^3} (mc)^3 \left(\frac{1}{\beta mc^2}\right)^{3/2} \sqrt{\frac{\pi}{2}} = V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{8.124}$$

which corresponds to the nonrelativistic case (cf. Example 7.12). Analogously, for very high temperatures $u = \beta mc^2 \ll 1$, with Equation (8.121) one finds from Equation (8.123), $K_2(u) \approx 2/u^2$, as well as $e^u \approx 1$:

$$Z(T, V, 1) \approx \frac{8\pi V}{h^3} (mc)^3 \left(\frac{1}{\beta mc^2}\right)^3 = 8\pi V \left(\frac{kT}{hc}\right)^3 \tag{8.125}$$

This is just the *partition function of the ultrarelativistic ideal gas*, which is here reproduced in the limit $kT \gg mc^2$—high temperatures, or small rest masses. The total partition function, according to Equation (8.113), is

$$Z(T, V, N) = \frac{1}{N!} \left[4\pi V \left(\frac{mc}{h}\right)^3 \exp\{\beta mc^2\} \frac{K_2(\beta mc^2)}{\beta mc^2} \right]^N \tag{8.126}$$

This can be used to calculate the free energy, where as usual we assume $N \gg 1$ and $\ln N! \approx N \ln N - N$, so that

$$\begin{aligned} F(T, V, N) &= -kT \ln Z(T, V, N) \\ &= -NkT \left[\ln \left\{ 4\pi \frac{V}{N} \left(\frac{mc}{h}\right)^3 \frac{K_2(u)}{u} e^u \right\} + 1 \right] \\ &= -NkT \left[\ln \left\{ 4\pi \frac{V}{N} \left(\frac{mc}{h}\right)^3 \frac{K_2(\beta mc^2)}{\beta mc^2} \right\} + 1 \right] - Nmc^2 \end{aligned} \tag{8.127}$$

For the pressure we get

$$p(T, V, N) = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{NkT}{V} \tag{8.128}$$

i.e., the ideal gas equation is also valid for the relativistic ideal gas. The chemical potential can be easily calculated, too,

$$\mu(T, V, N) = \left.\frac{\partial F}{\partial N}\right|_{T,V} = -kT \ln\left\{4\pi \frac{V}{N}\left(\frac{mc}{h}\right)^3 \frac{K_2(\beta mc^2)}{\beta mc^2}\right\} - mc^2 \tag{8.129}$$

Here we want to add a short remark. Since in Equation (8.112) we explicitly subtracted the rest mass of the particles, in Equation (8.123) there appears the factor $e^u = \exp\{\beta mc^2\}$. This means that in the free energy (8.127) the rest energy Nmc^2 of all particles is subtracted, so that only the kinetic energy of the particle remains. For the same reason, in Equation (8.129) there appears the term mc^2. This has the advantage that all results reproduce the nonrelativistic results in the limiting case $T \to 0$.

However, one can also drop the factor e^u. This would mean all energies contain a contribution due to the rest masses of the particles. Then in Equation (8.129) the term $-mc^2$ would drop out, and the chemical potential would just increase by this value. In a strictly relativistic consideration this is, of course, reasonable because the minimum energy which is required to add another particle to the system in equilibrium (chemical potential), is just the rest mass of the particle.

The entropy of the relativistic ideal gas is a little more difficult to calculate. We have

$$S(T, V, N) = -\left.\frac{\partial F}{\partial T}\right|_{N,V} = Nk\left[\ln\left\{4\pi \frac{V}{N}\left(\frac{mc}{h}\right)^3 \frac{K_2(\beta mc^2)}{\beta mc^2}\right\} + 1\right] + NkT\left[\frac{u}{K_2(u)}\left(\frac{K_2'(u)}{u} - \frac{K_2(u)}{u^2}\right)\frac{du}{dT}\right] \tag{8.130}$$

with

$$\frac{du}{dT} = \frac{d}{dT}(\beta mc^2) = -\frac{mc^2}{kT^2} = -\frac{u}{T} \tag{8.131}$$

We can calculate the derivative of the K_2-function with the aid of a recursion formula:

$$K_n'(u) = -K_{n-1}(u) - \frac{n}{u}K_n(u) \tag{8.132}$$

Inserting this into Equation (8.130), we obtain

$$\begin{aligned} S(T, V, N) &= Nk\left[\ln\left\{4\pi \frac{V}{N}\left(\frac{mc}{h}\right)^3 \frac{K_2(u)}{u}\right\} + 1\right] + Nk\left[u\frac{K_1(u)}{K_2(u)} + 3\right] \\ &= Nk\left[\ln\left\{4\pi \frac{V}{N}\left(\frac{mc}{h}\right)^3 \frac{K_2(u)}{u}\right\} + 4 + u\frac{K_1(u)}{K_2(u)}\right] \end{aligned} \tag{8.133}$$

Here we can also reproduce the nonrelativistic result in the limit $u \gg 1$. For $u \gg 1$ in the first term of Equation (8.133) we have $K_2(u)/u \approx \sqrt{\pi/2}u^{-3/2}e^{-u}$. The factor $u^{-3/2}$

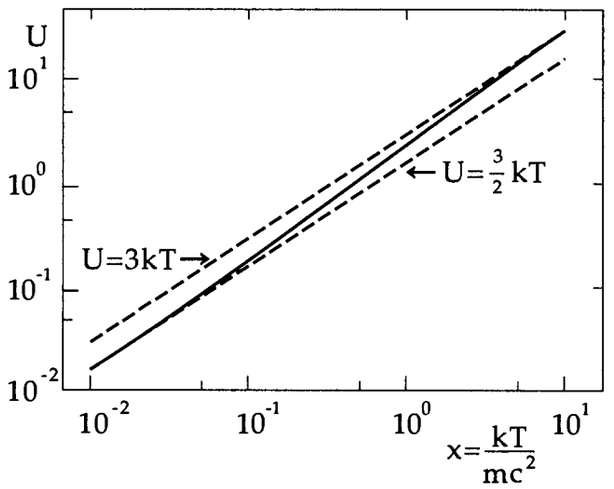


Figure 8.17. Internal energy of a relativistic ideal gas.

together with the other factors just yields $\frac{V}{N\lambda^3}$, the nonrelativistic argument of the logarithm. The term $\ln e^{-u} = -u$ together with $uK_1(u)/K_2(u) \approx u(1 + \frac{3}{8u} + \cdots)/(1 + \frac{15}{8u} + \cdots) \approx u - \frac{3}{2} + \cdots$ yields a constant contribution $4 - 3/2 = 5/2$, thus just the term which is missing in the nonrelativistic entropy (cf. Equation (7.52)).

In the same way, the ultrarelativistic limit in Equation (8.133) for $u \ll 1$ can be checked. Then $uK_1(u)/K_2(u) \approx u^2/2 \approx 0$ and $K_2(u)/u \approx 2/u^3$, which just yields the right argument in the logarithm. (cf. Exercise 7.2). From Equations (8.127) and (8.133) the internal energy (Figure 8.16) is calculated to be

$$U(T, V, N) = F + TS = NkT\left[3 + u\frac{K_1(u)}{K_2(u)}\right] - Nmc^2$$

$$= Nmc^2\left[\frac{K_1(u)}{K_2(u)} + \frac{3}{u} - 1\right] \tag{8.134}$$

Here $u \to \infty$ yields the nonrelativistic limit $U \approx \frac{3}{2}NkT$, too, while for $u \to 0$ we have $K_1(u)/K_2(u) \approx u/2$, so that $U \approx Nmc^2 3/u = 3NkT$. The internal energy therefore continually increases from the nonrelativistic case $\frac{3}{2}NkT$ for small T up to the asymptotic ultrarelativistic case $U = 3NkT$. Equation (8.134) yields for the specific heat

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = -\frac{u}{T}\left.\frac{\partial}{\partial u}U\right|_V$$

$$= -Nmc^2\frac{u}{T}\left\{\frac{K_1'(u)}{K_2(u)} - \frac{K_1(u)K_2'(u)}{K_2^2(u)} - \frac{3}{u^2}\right\}$$

$$= \frac{Nmc^2}{T}\left\{u\frac{K_0(u)}{K_2(u)} - \frac{K_1(u)}{K_2(u)}\left(1 + u\frac{K_1(u)}{K_2(u)}\right) + \frac{3}{u}\right\} \tag{8.135}$$

where again we have used the recursion formula (8.132).

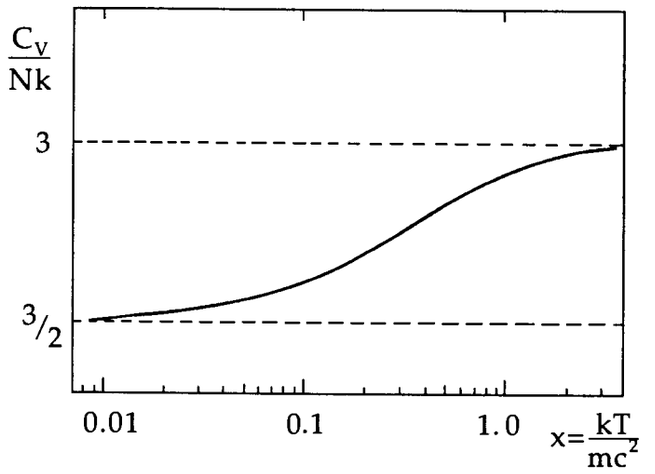


Figure 8.18. Specific heat of the relativistic gas.

The expression (8.135) can still be simplified a little, if one uses the recursion formula

$$K_{n-1} = K_{n+1} - \frac{2}{u} K_n \tag{8.136}$$

Inserting Equation (8.136) into Equation (8.135) for $n - 1 = 0$, we get

$$C_V = \frac{Nmc^2}{T} \left\{ u + \frac{3}{u} - \frac{K_1(u)}{K_2(u)} \left(3 + u \frac{K_1(u)}{K_2(u)} \right) \right\} \tag{8.137}$$

In Equation (8.137) only the ratio $K_1(u)/K_2(u)$ remains to be calculated, which is a considerable simplification compared to Equation (8.135). Using the approximations

$$\frac{K_1(u)}{K_2(u)} \approx 1 - \frac{3}{2u} + \frac{240}{128u^2} + \frac{1455}{1024u^3} + \cdots \qquad u \gg 1 \tag{8.138}$$

and

$$\frac{K_1(u)}{K_2(u)} \approx \frac{u}{2} + \cdots \qquad u \ll 1 \tag{8.139}$$

we can again reproduce the nonrelativistic case $C_V = \frac{3}{2} Nk$ and the ultrarelativistic case $C_V = 3Nk$ from Equation (8.137). (See Figure 8.18.)

Now we want to add a warning for the calculation with expansions. It is essential to take care that one always considers all terms up to a certain order of the expansion parameter consistently. For instance, if one wants to evaluate Equation (8.135) for $u \gg 1$ up to the order u^{-2}, then $K_1(u)/K_2(u)$ is necessary up to the third order, since there appears a term $uK_1(u)/K_2(u)$, etc.

9 The Macrocanonical Ensemble

Having studied in great detail the microcanonical and canonical ensembles, we now turn to the so-called *macrocanonical ensemble* (also *grand canonical ensemble*), which is very important for applications. The phase-space density within an ensemble denotes the probability density of finding the system in a certain microstate compatible with the given macrostate. The microcanonical ensemble describes closed systems with given E, V, and N, while the canonical ensemble describes systems in a heat bath, i.e., with given T, V, and N.

Now we want to consider *open systems*, in which heat *and* particles can be exchanged with the surroundings. Here T, V, and μ are the independent variables. A certain chemical potential is established, in analogy to temperature in a heat bath, by a large particle reservoir which is in contact with the system. If the particle reservoir is sufficiently large, the value of the chemical potential depends exclusively on the properties of the reservoir. The system under consideration no longer has a certain particle number, since particles are continually exchanged between system and reservoir. A mean value and a most probable value of particle number will be established, just as a mean energy and a most probable energy were established for a given temperature.

Systems at a given T, V, and μ are of great practical interest. Consider a fluid which is in equilibrium with its vapor at a given temperature (the system *fluid* + *vapor* being in a heat bath). Then molecules will continually pass from the fluid into the gaseous phase and vice versa. Now the total system (heat bath+fluid+vapor) could be described by the microcanonical ensemble, or the system (fluid+vapor) could be described by the canonical ensenble. However, if one is interested only in the properties of one of the phases, this would be most inconvenient—thus one switches over to the macrocanonical ensemble.

To this end, we must first determine the phase-space density of a system at a given T, V, and μ. Not only must the phase-space density denote the probability to be in a phase space with a certain particle number N, but it must also denote the probability that the system contains just N particles, since now in principle all particle numbers $N = 0, 1, 2, \ldots, \infty$ are allowed. To determine this probability distribution, one proceeds analogously to the case of the canonical ensemble (cf. Chapter 7):

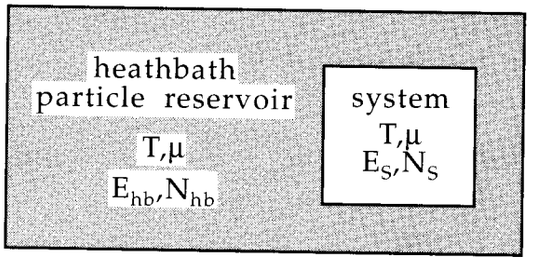


Figure 9.1. Scheme of the system under consideration.

First we apply the concept of the microcanonical ensemble to the total system. The total energy

$$E = E_S + E_R \tag{9.1}$$

has a fixed value. Also, the total particle number is constant:

$$N = N_S + N_R \tag{9.2}$$

We require that the reservoir must be very large compared to the system,

$$\frac{E_S}{E} = \left(1 - \frac{E_R}{E}\right) \ll 1, \qquad \frac{N_S}{N} = \left(1 - \frac{N_R}{N}\right) \ll 1 \tag{9.3}$$

The system S can assume all possible particle numbers $N_S \in [0, 1, \ldots N]$ and all possible energies $E_S \in [0, \ldots, E]$. If it is in a certain microstate, characterized by a certain particle number N_S and a certain phase-space point i with the energy $E_S = E_i$, the reservoir still has at its disposal a large number Ω_r of different microstates with the energy $E_R = E - E_i$ and the particle number $N_R = N - N_s$. The probability p_{i,N_S} of finding the system in the microstate i with the particle number N_s will be proportional to this number $\Omega_R(E_r, N_r) = \Omega_R(E - E_i, N - N_S)$ of possibilities,

$$p_{i,N} \propto \Omega_R(E_R, N_R) = \Omega_R(E - E_i, N - N_S) \tag{9.4}$$

Because of the assumption (9.3), one can expand with respect to the small quantities E_i, and N_S. To be able to identify the derivatives which occur in this procedure, we first expand $\ln \Omega_R$:

$$k \ln \Omega_R(E - E_i, N - N_S) = k \ln \Omega_R(E, N) - \frac{\partial}{\partial E}(k \ln \Omega_R(E, N))\, E_i - \frac{\partial}{\partial N}(k \ln \Omega_R(E, N))\, N_S + \cdots \tag{9.5}$$

we have:

$$\frac{\partial}{\partial E}(k \ln \Omega_R(E, N)) = \frac{\partial S_R}{\partial E} = \frac{1}{T} \tag{9.6}$$

$$\frac{\partial}{\partial N}(k \ln \Omega_R(E, N)) = \frac{\partial S_R}{\partial N} = -\frac{\mu}{T} \tag{9.7}$$

If we restrict ourselves to the terms denoted in Equation (9.5), insertion and exponentiation lead to

$$\Omega_R(E - E_i, N - N_S) \propto \Omega_R(E, N) \exp\left\{-\frac{E_i}{kT} + \frac{\mu N_S}{kT}\right\} \tag{9.8}$$

or, since $\Omega_R(E, N)$ is only a constant factor,

$$p_{i,N_S} \propto \exp\left\{-\frac{E_i}{kT} + \frac{\mu N_S}{kT}\right\} \tag{9.9}$$

The lacking proportionality factor can be determined from the normalization $\sum_{N_S} \sum_i p_{i,N_S} = 1$,

$$p_{i,N} = \frac{\exp\{-\beta (E_i - \mu N)\}}{\sum_N \sum_i \exp\{-\beta (E_i - \mu N)\}} \tag{9.10}$$

Here we have dropped the subscript S on the particle number, since we are no longer in danger of confusion. Just like in the canonical ensemble, the sum over i extends over all microstates i in phase space with particle number N.

The distribution (9.10) is the desired probability of finding a system in a microstate i with the energy E_i and the particle number N at given T and μ. The corresponding phase-space density can be found by switching over to the continuous formulation,

$$\rho_{gc}(N, q_\nu, p_\nu) = \frac{\exp\{-\beta (H(q_\nu, p_\nu) - \mu N)\}}{\sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d^{3N}q \int d^{3N}p \exp\{-\beta (H(q_\nu, p_\nu) - \mu N)\}} \tag{9.11}$$

The phase-space density given in Equations (9.11) or (9.10) is called the *macrocanonical distribution.* Before we examine this distribution in greater detail, we want to derive it once again with the aid of ensemble theory, and we want to show that Equation (9.10) or Equation (9.11) is the most probable distribution for a given T and μ.

To do this, we consider again an ensemble of $\mathcal{N}$ identical systems at given T, V, and μ. At a given time, each of these systems will have a certain particle number N and be at a certain phase-space point.

Now we divide all phase spaces of $N = 1, 2, \ldots$ into equally large cells $\Delta\omega_{i,N}$ which are enumerated by i and N. The index i runs through all phase-space cells in the phase space of particle number N. In each of these phase-space cells there will be a certain number $n_{i,N}$ of systems of our ensemble, and we now want to calculate the most probable distribution $\{n^*_{i,N}\}$.

The numbers $n_{i,N}$ must fulfill three constraints. First, the total number $\mathcal{N}$ of the systems is fixed:

$$\sum_{i,N} n_{i,N} = \mathcal{N} \tag{9.12}$$

Second at a given temperature, the systems no longer have a fixed energy, but the mean value of all energies E_i over all phase-space cells has a certain value:

$$\sum_{i,N} n_{i,N} E_i = \mathcal{N} \langle E_i \rangle = \mathcal{N} U \tag{9.13}$$

Conditions (9.12) and (9.13) are already known from the canonical ensemble. Now there is another condition, because the particle number N no longer has a fixed value, but in equilibrium there is established a certain mean particle number $\langle N \rangle$:

$$\sum_{i,N} n_{i,N} N = \mathcal{N} \langle N \rangle \tag{9.14}$$

We can directly bring over the probability of a given distribution $\{n_{i,N}\}$ from the canonical or microcanonical case,

$$W\{n_{i,N}\} = \mathcal{N}! \prod_{i,N} \frac{(\omega_{i,N})^{n_{i,N}}}{n_{i,N}!} \tag{9.15}$$

but now the phase-space cells are enumerated by two indices. Here again $\omega_{i,N}$ is the probability of finding *one* microstate in the cell $\Delta\omega_{i,N}$. The most probable distribution $\{n^*_{i,N}\}$ is found just as in the former case. We form

$$\ln W\{n_{i,N}\} = \mathcal{N} \ln \mathcal{N} - \mathcal{N} - \sum_{i,N} \left\{ \left(n_{i,N} \ln n_{i,N} - n_{i,N} \right) - n_{i,N} \ln \omega_{i,N} \right\} \tag{9.16}$$

and search the extreme value with respect to the $n_{i,N}$, where we eliminate the constraints (9.12–14) with the aid of three Lagrange multipliers λ, $-\beta$, and α:

$$d \ln W\{n_{i,N}\} = -\sum_{i,N} \left\{ \ln n_{i,N} - \ln \omega_{i,N} \right\} dn_{i,N} = 0 \tag{9.17}$$

$$\lambda \sum_{i,N} dn_{i,N} = 0 \tag{9.18}$$

$$-\beta \sum_{i,N} E_i \, dn_{i,N} = 0 \tag{9.19}$$

$$\alpha \sum_{i,N} N \, dn_{i.N} = 0 \tag{9.20}$$

If one adds up these equations, it follows that

$$\sum_{i,N} \left(\ln n_{i,N} - \ln \omega_{i,N} - \lambda + \beta E_i - \alpha N \right) dn_{i,N} = 0 \tag{9.21}$$

Here all of the $dn_{i,N}$ may be assumed to be independent of each other, so that the coefficients must vanish, if afterwards α, β, and λ are determined such that the constraints are fulfilled:

$$n^*_{i,N} = \omega_{i,N} e^{\lambda} \exp\{-\beta E_i + \alpha N\} \tag{9.22}$$

The quantity λ is determined from Equation (9.12), where *we again assume the probabilities* $\omega_{i,N}$ *for equally sized phase-space cells to be identical*:

$$\frac{n^*_{i,N}}{\mathcal{N}} = \frac{\exp\{-\beta E_i + \alpha N\}}{\sum_{i,N} \exp\{-\beta E_i + \alpha N\}} \tag{9.23}$$

while β and α must be determined from Equations (9.13) and (9.14):

$$U = \frac{\sum_{i,N} E_i \exp\{-\beta E_i + \alpha N\}}{\sum_{i,N} \exp\{-\beta E_i + \alpha N\}} \tag{9.24}$$

$$\langle N \rangle = \frac{\sum_{i,N} N \exp\{-\beta E_i + \alpha N\}}{\sum_{i,N} \exp\{-\beta E_i + \alpha N\}} \tag{9.25}$$

For the determination of α and β, however, we want to use again the well-known prescription using the entropy. In the continuous formulation, Equation (9.23) reads

$$\rho_{gc}(N, q_\nu, p_\nu) = \frac{\exp\{-\beta H(q_\nu, p_\nu) + \alpha N\}}{\sum_{N=1}^{\infty} \frac{1}{h^{3N}} \int d^{3N}q \int d^{3N}p \exp\{-\beta H(q_\nu, p_\nu) + \alpha N\}} \tag{9.26}$$

In analogy to the canonical case, the denominator is again written as

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d^{3N}q \int d^{3N}p \exp\{-\beta H(q_\nu, p_\nu) + \alpha N\} \tag{9.27}$$

Now $\mathcal{Z}$ is called the *macrocanonical partition function.* We will soon see that its significance is analogous to the canonical partition function Z.

We know that in general the entropy can be written as an ensemble average,

$$S = \langle -k \ln \rho \rangle \tag{9.28}$$

For the macrocanonical distribution, Equation (9.28) reads explicitly

$$S(\beta, V, \alpha) = \sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d^{3N}q \int d^{3N}p \rho_{gc}(N, q_\nu, p_\nu) [k \ln \mathcal{Z} + k\beta H(q_\nu, p_\nu) - k\alpha N] \tag{9.29}$$

In the formation of ensemble averages now we not only have to integrate over all phase-space points, but we must also sum over all possible particle numbers.

The first term in the square brackets in Equation (9.29) neither depends on the phase-space point nor on the particle number; therefore it can be drawn out of the integral, so that there remains only the normalization integral of ρ_{gc}. The second term simply yields the definition of the mean value of the energy,

$$\langle H(q_\nu, p_\nu) \rangle = \sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d^{3N}q \int d^{3N}p \rho_{gc}(N, q_\nu, p_\nu) H(q_\nu, p_\nu) \tag{9.30}$$

and the last term correspondingly is the mean particle number

$$\langle N \rangle = \sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d^{3N}q \int d^{3N}p \rho_{gc}(N, q_\nu, p_\nu) N \tag{9.31}$$

Therefore Equation (9.29) can also be written as

$$S(\beta, V, \alpha) = k \ln \mathcal{Z}(\beta, V, \alpha) + k\beta \langle H \rangle - k\alpha \langle N \rangle \tag{9.32}$$

This equation is the analogy of Equation (7.27). If one identifies the mean energy $\langle H \rangle$ with the thermodynamic energy U, and correspondingly, the mean particle number $\langle N \rangle$ with the thermodynamic particle number, then α and β can be read off from Equation (9.32). We must take care of the fact that β is a function of U and α (according to Equation (9.24)), and equally, α is a function of $\langle N \rangle$ and β (Equation (9.25)),

$$\frac{\partial S}{\partial U} = \frac{\partial \beta}{\partial U} \frac{\partial}{\partial \beta} k \ln \mathcal{Z}(\beta, V, \alpha) + k \frac{\partial \beta}{\partial U} U + k\beta \tag{9.33}$$

We have to take into account that $\ln \mathcal{Z}(\beta, V, \alpha)$ must only be differentiated with respect to the explicit β dependence, but not with respect to the implicit dependence in $\alpha(\beta, \langle N \rangle)$. This is because α does not depend on U, with respect to which $k \ln \mathcal{Z}$ originally had to be differentiated. One can easily convince oneself that $\partial k \ln \mathcal{Z}/\partial\beta = -kU$, and thus that

$$\frac{\partial S}{\partial U} = \frac{1}{T} = k\beta, \qquad \Rightarrow \beta = \frac{1}{kT} \tag{9.34}$$

Furthermore we have

$$\frac{\partial S}{\partial \langle N \rangle} = \frac{\partial \alpha}{\partial \langle N \rangle} \frac{\partial}{\partial \alpha} k \ln \mathcal{Z}(\beta, V, \alpha) - k \frac{\partial \alpha}{\partial \langle N \rangle} \langle N \rangle - k\alpha \tag{9.35}$$

and with $\partial k \ln \mathcal{Z}/\partial\alpha = k \langle N \rangle$ (again we must take care only of the explicit α dependence) there follows because of $\mathrm{d}S = \frac{\mathrm{d}U}{T} + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N$ (cf. e.g., Equation (3.1)):

$$\frac{\partial S}{\partial \langle N \rangle} = -\frac{\mu}{T} = -k\alpha \Rightarrow \alpha = \frac{\mu}{kT} \tag{9.36}$$

which identifies α and β. Let us now recall the macrocanonical potential in Equation (4.111). Thus, Equation (9.32) serves us even further. If we insert α and β and rewrite it a little, we get

$$U - TS - \mu \langle N \rangle = -kT \ln \mathcal{Z}(T, V, \mu) \tag{9.37}$$

Because of Equation (4.111), we can calculate the *macrocanonical potential ϕ from the macrocanonical partition function* according to

$$\phi(T, V, \mu) = -kT \ln \mathcal{Z}(T, V, \mu) \tag{9.38}$$

From thermodynamics, we know already that the macrocanonical potential ϕ for a system at given T, V, and μ has the same significance as the free energy F for a system at given T, V, and N, or as the entropy S for a closed system at E, V, and N. The knowledge of the macrocanonical partition function therefore allows for the calculation of all thermodynamic properties of the system.

Because of the central significance of the macrocanonical partition function $\mathcal{Z}$, we want to write it down once again. Just as in the canonical case, the Gibbs correction factor $1/N!$ must be added in the calculation of $\mathcal{Z}$ for *indistinguishable particles*:

$$\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int d^{3N}q \int d^{3N}p \exp\{-\beta (H(q_\nu, p_\nu) - \mu N)\} \tag{9.39}$$

This factor ensures that microstates differing only by a different enumeration of the N particles are not counted as different microstates. In the case of *distinguishable particles* this factor does not occur. Using Equation (9.39), we find a very important relation with the canonical partition function:

$$\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{\infty} \left(\exp\left\{\frac{\mu}{kT}\right\}\right)^N Z(T, V, N) \tag{9.40}$$

Therefore, the macrocanonical partition function is nothing but a *weighted sum of all canonical partition functions*. The weighting factor $z = \exp\{\mu/kT\}$ is called the *fugacity*. In

Equation (9.40) we recognize again, very clearly, the principle which connects the microcanonical, canonical, and macrocanonical ensembles: as we know, the canonical partition function Z was formed as the sum of all microcanonical "partition functions" g at energy E, particle number N, and volume V, weighted by the Boltzmann factor $\exp\{-\beta E\}$:

$$Z(\beta, N, V) = \sum_E \exp\{-\beta E\} g(E, N, V) \tag{9.41}$$

where the energy E is now no longer a fixed quantity, but only its mean value $\langle E \rangle = U$ is fixed. On the other hand, the temperature $T = (k\beta)^{-1}$ has a fixed value given by the heat bath.

The macrocanonical partition function $\mathcal{Z}$ results as the sum of all canonical partition functions Z at temperature T, volume V, and particle number N weighted by $\exp\{\beta\mu N\}$ (Equation (9.40)). However, the particle number N also is no longer fixed, but has only a mean value, and the chemical potential μ has a fixed value given by the particle bath.

In general, Equation (9.40) can be evaluated for noninteracting systems. For such systems we have (indistinguishable particles):

$$Z(T, V, N) = \frac{1}{N!} [Z(T, V, 1)]^N \tag{9.42}$$

If one inserts this into Equation (9.40), one obtains

$$\begin{aligned} \mathcal{Z}(T, V, \mu) &= \sum_{N=0}^{\infty} \frac{1}{N!} \left[\exp\left\{\frac{\mu}{kT}\right\} Z(T, V, 1)\right]^N \\ &= \exp\left\{\exp\left\{\frac{\mu}{kT}\right\} Z(T, V, 1)\right\} \end{aligned} \tag{9.43}$$

Thus, we can directly write down $\mathcal{Z}(T, V, \mu)$ for many problems which we have already treated in the canonical formalism. As an example we will show that for the ideal gas the macrocanonical ensemble yields just the same results as the other two.

Example 9.1: The ideal gas in the macrocanonical ensemble

The calculation of $\mathcal{Z}(T, V, \mu)$ is conveniently done according to Equation (9.43). For an ideal gas (Example 7.1) we have

$$Z(T, V, 1) = \frac{V}{\lambda^3}$$

with

$$\lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$

and thus

$$\mathcal{Z}(T, V, \mu) = \exp\left\{\exp\left\{\frac{\mu}{kT}\right\} V \left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\}$$

The macrocanonical potential is therefore

$$\phi(T, V, \mu) = -kT \ln \mathcal{Z}(T, V, \mu) = -kT \exp\left\{\frac{\mu}{kT}\right\} V \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

This immediately yields the equations of state:

$$-\left.\frac{\partial \phi}{\partial T}\right|_{V,\mu} = S(T, V, \mu) = \exp\left\{\frac{\mu}{kT}\right\} V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} k\left[\frac{5}{2} - \frac{\mu}{kT}\right] \tag{9.44}$$

$$-\left.\frac{\partial \phi}{\partial V}\right|_{T,\mu} = p(T, V, \mu) = kT \exp\left\{\frac{\mu}{kT}\right\} \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{9.45}$$

$$-\left.\frac{\partial \phi}{\partial \mu}\right|_{T,V} = N(T, V, \mu) = \exp\left\{\frac{\mu}{kT}\right\} V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{9.46}$$

If one inserts Equation (9.46) into Equations (9.45) and (9.44), one obtains the ideal gas equation and the well-known entropy $S(T, V, N)$ of the ideal gas.

We want to write Equation (9.38) in another way. The potential ϕ is defined by

$$\phi = U - TS - \mu N \tag{9.47}$$

Because of the Euler relation (cf. Equation (2.72)),

$$U = TS - pV + \mu N \tag{9.48}$$

Equations (9.47) or (9.38) can also be formulated as follows:

$$-\frac{\phi}{kT} = \frac{pV}{kT} = \ln \mathcal{Z} \tag{9.49}$$

In the case of the ideal gas, $\ln \mathcal{Z} = N$, as one can see from Example 9.1. The significance of Equation (9.49) is that $\ln \mathcal{Z}$ for real gases often can be approximately calculated by a series expansion (cf. Part IV). Equation (9.49) then directly gives the thermal equation of state of this gas.

At the end of this section we still want to remark that our prescription for deriving the macrocanonical partition function has a very general character, and in special cases may serve to derive different practical equations of state. Namely, we know very well the mathematical operation which connects all partition functions: it is just the Laplace transformation! Sometimes it may be advantageous to consider other thermodynamic variables instead of (E, V, N), (T, V, N), or (T, V, μ), e.g., (T, p, N). Then the respective partition function is obtained through another Laplace transformation, in our example just a Laplace transformation of the canonical partition function:

$$\Xi(T, p, N) = \sum_V \exp\{-\gamma V p\} Z(T, V, N) \tag{9.50}$$

with a Lagrange multiplier γ. This partition function is especially convenient in systems with a given temperature, particle number, and pressure. Here, the volume is no longer fixed, but at a constant pressure a mean value of the volume, $\langle V \rangle$, will be established.

Just as the logarithm of all partition functions treated up to now could be related to thermodynamic potentials, i.e.,

$$\begin{aligned} g &\leftrightarrow S = k \ln g \\ Z &\leftrightarrow F = -kT \ln Z \\ \mathcal{Z} &\leftrightarrow \phi = -kT \ln \mathcal{Z} \end{aligned} \tag{9.51}$$

Ξ can also be related to a potential: let ρ_Ξ denote the phase-space density related to Ξ,

$$\rho_\Xi = \frac{\exp\{-\beta H - \gamma p V\}}{\sum_V \int d^{3N}q \int d^{3N}p \frac{1}{h^{3N}} \exp\{-\beta H - \gamma p V\}} \tag{9.52}$$

Then we have

$$\begin{aligned} S = \langle -k \ln \rho_\Xi \rangle &= \sum_V \int \frac{d^{3N}q\, d^{3N}p}{h^{3N}} \rho_\Xi \{k \ln \Xi(T, p, N) + k\beta H + k\gamma p V\} \\ &= k \ln \Xi + k\beta \langle H \rangle + k\gamma p \langle V \rangle \end{aligned} \tag{9.53}$$

or $-kT \ln \Xi = U - TS + k\gamma T p \langle V \rangle$. By a procedure analogous to the one performed in the case of $\mathcal{Z}$, one can identify γ with β, and one obtains:

$$G = -kT \ln \Xi \tag{9.54}$$

thus, the *Gibbs' free enthalpy* is the thermodynamic potential corresponding to Ξ (cf. Chapter 4).

Fluctuations in the macrocanonical ensemble

In the preceding section we calculated the probability $p_{i,N}$ of finding a system of the macrocanonical ensemble just at a particle number N and in the phase-space point i:

$$p_{i,N} = \frac{1}{\mathcal{Z}} \exp\{-\beta (E_i - \mu N)\} \tag{9.55}$$

Here E_i is the energy corresponding to the phase-space cell i, and $\mathcal{Z}$ is the macrocanonical partition function

$$\mathcal{Z} = \sum_{i,N} \exp\{-\beta (E_i - \mu N)\} \tag{9.56}$$

From Equation (9.55) we can, in analogy to the canonical ensemble, calculate the probability density $p(E, N)$ of finding a system of the ensemble at energy E (no matter which microstate i) and at particle number N: If $g_N(E)$ is the number of microstates i in the energy interval $E, E + dE$ at particle number N, then

$$p(E, N) = \frac{1}{\mathcal{Z}} g_N(E) \exp\{-\beta (E - \mu N)\} \tag{9.57}$$

and the macrocanonical partition function is given by

$$\mathcal{Z} = \sum_{N=1}^{\infty} \int_0^{\infty} dE g_N(E) \exp\{-\beta (E - \mu N)\} \tag{9.58}$$

In the case of fixed particle number N, the distribution of the energies in the macrocanonical ensemble is therefore the same as in the canonical ensemble. In addition, however, there is still a distribution in the particle number N. Again, we can calculate the most probable values for the energy and the particle number:

$$\left.\frac{\partial p(E, N)}{\partial E}\right|_{E=E^*} = 0 \Rightarrow \left.\frac{\partial g_N(E)}{\partial E}\right|_{E=E^*} = \beta g_N(E^*) \tag{9.59}$$

Because $g_N(E) \approx \Omega(E, V, N)/\Delta E$, the most probable energy of the macrocanonical ensemble, just as in the canonical case, is given by

$$\left.\frac{\partial S}{\partial E}\right|_{E=E^*} = \frac{1}{T} \tag{9.60}$$

and is thus identical to the fixed energy of the microcanonical case. The most probable particle number N^* must obey

$$\left.\frac{\partial p(E, N)}{\partial N}\right|_{N=N^*} = 0 \Rightarrow \left.\frac{\partial g_N(E)}{\partial N}\right|_{N=N^*} = -\beta \mu g_N(E) \tag{9.61}$$

or

$$\left.\frac{\partial S}{\partial N}\right|_{N=N^*} = -\frac{\mu}{T} \tag{9.62}$$

i.e., N^* is also identical to the given particle number N of the microcanonical case. Even in analogy to the canonical case, we have $N^* = \langle N \rangle = N_{mc}$, and $E^* = \langle E \rangle = E_{mc}$, because

$$\langle E \rangle = \phi + TS + \mu N \tag{9.63}$$

The mean energy results from the reverse Legendre transformation of ϕ and coincides with the thermodynamic internal energy U, and thus also with the fixed energy E given in the microcanonical case. Correspondingly, we can conclude for the mean particle number:

$$\begin{aligned} \langle N \rangle &= \sum_{i,N} N p_{i,N} = \frac{1}{\mathcal{Z}} \sum_{i,N} N \exp\{-\beta (E_i - \mu N)\} \\ &= \frac{\partial}{\partial \mu} (kT \ln \mathcal{Z})_{T,V} = -\left.\frac{\partial \phi}{\partial \mu}\right|_{T,V} \end{aligned} \tag{9.64}$$

The mean particle number $\langle N \rangle$ is identical to the thermodynamic particle number $N = -\partial\phi/\partial\mu|_{T,V}$, which was equal to the fixed given particle number of the microcanonical ensemble. The deviations of the mean values in the macrocanonical ensemble are given by the standard deviations of the distributions,

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 \tag{9.65}$$

One has

$$\langle N^2\rangle = \sum_{i,N} N^2 p_{i,N} = \frac{1}{\mathcal{Z}} \sum_{i,N} N^2 \exp\{-\beta (E_i - \mu N)\} = \frac{(kT)^2}{\mathcal{Z}} \frac{\partial^2}{\partial \mu^2} \mathcal{Z}\Big|_{T,V} \tag{9.66}$$

or, because $kT\partial\mathcal{Z}/\partial\mu|_{T,V} = \mathcal{Z} \cdot \langle N\rangle$,

$$\langle N^2\rangle = \frac{kT}{\mathcal{Z}} \frac{\partial}{\partial \mu} (\mathcal{Z} \cdot \langle N\rangle)_{T,V} = \langle N\rangle^2 + kT \left.\frac{\partial \langle N\rangle}{\partial \mu}\right|_{T,V} \tag{9.67}$$

$$\sigma_N^2 = kT \left.\frac{\partial \langle N\rangle}{\partial \mu}\right|_{T,V} = kT \left.\frac{\partial N}{\partial \mu}\right|_{T,V} \tag{9.68}$$

In the last equation, $\langle N\rangle$ has been replaced by the thermodynamic particle number N. The thermodynamic quantity $\partial N/\partial\mu|_{T,V}$ can be replaced by the compressibility κ of the system.

The Gibbs–Duhem relation (2.74) for the intensive state variables

$$d\mu = v\, dp - s\, dT \tag{9.69}$$

with $v = V/N$ and $s = S/N$, in the case of constant temperature and volume, leads to

$$\left.\frac{\partial \mu}{\partial v}\right|_T = v \left.\frac{\partial p}{\partial v}\right|_T \tag{9.70}$$

Now we interpret T, V, and N as independent variables. The pressure is then a function of these variables, $p(T, V, N)$. However, pressure and temperature are intensive quantities of state, while volume and particle number are extensive ones. Therefore, the pressure cannot depend on the quantities V and N individually, but only on the intensive combination $v = V/N$. Hence the function $p(T, V, N)$ must have the special form $p(T, V/N)$ or $p(T, v)$. This is, of course, a consequence of the zero order homogeneity of the intensive quantites of state. The special form of the pressure $p(T, V/N)$ now allows us to rewrite the derivative with respect to N on the right side of Equation (9.70) as a derivative with respect to V: namely, according to the chain rule, we have

$$\begin{aligned}\left.\frac{\partial}{\partial N} p(T, V/N)\right|_{T,V} &= \left.\frac{\partial}{\partial \left(\frac{V}{N}\right)} p(T, V/N)\right|_T \times \left.\frac{\partial \left(\frac{V}{N}\right)}{\partial N}\right|_V \\ &= -\frac{V}{N^2} \left.\frac{\partial}{\partial \left(\frac{V}{N}\right)} p(T, V/N)\right|_T \end{aligned} \tag{9.71}$$

On the other hand, the derivative with respect to the volume at constant N reads

$$\begin{aligned}\left.\frac{\partial}{\partial V} p(T, V/N)\right|_{T,N} &= \left.\frac{\partial}{\partial \left(\frac{V}{N}\right)} p(T, V/N)\right|_T \times \left.\frac{\partial \left(\frac{V}{N}\right)}{\partial V}\right|_N \\ &= \frac{1}{N} \left.\frac{\partial}{\partial \left(\frac{V}{N}\right)} p(T, V/N)\right|_T \end{aligned} \tag{9.72}$$

Comparing Equations (9.71) and (9.72) we obtain the identity

$$\left.\frac{\partial p}{\partial N}\right|_{T,V} = -\frac{V}{N} \left.\frac{\partial p}{\partial V}\right|_{T,N} \tag{9.73}$$

Inserting this into the right-hand side of Equation (9.70) yields

$$\left.\frac{\partial \mu}{\partial N}\right|_{T,V} = -\left(\frac{V}{N}\right)^2 \left.\frac{\partial p}{\partial V}\right|_{T,N} \tag{9.74}$$

The derivative of the chemical potential can thus be expressed by the compressibility $\kappa = -\frac{1}{V}\,\partial V/\partial p|_{T,N}$. Insertion of Equation (9.74) into (9.68) yields the final result

$$\frac{\sigma_N^2}{N^2} = \frac{kT}{V}\kappa \qquad \text{or} \qquad \frac{\sigma_N}{N} = \sqrt{\frac{kT}{V}\kappa} \tag{9.75}$$

Since compressibility is an intensive quantity, the relative fluctuations of particle number with respect to N vanish for large volumes like $1/\sqrt{V}$, or, in the thermodynamic limit ($N \to \infty$, $V \to \infty$, $N/V = \text{const.}$), like $O(1/\sqrt{N})$. For systems with very large particle numbers, deviations from the mean value in the macrocanonical ensemble are vanishingly small.

However, this is true only as long as the compressibility has a finite value. An exception is, for instance, the phase transition gas–fluid. In the case of the Maxwell construction (Chapter 3), we have noticed that the isotherms in the pV diagram in the phase-coexistence region run horizontally, which corresponds to an infinitely large compressibility. There, and especially at the critical point of the gas, the fluctuations in particle number of both phases become very large, which is also observed experimentally in the form of *opalescence* at the critical point. The large fluctuations correspond to the short-time condensation of gas to fluid droplets, which however, can again evaporate. These fluctuations become especially large at the critical point, where we have $\rho_{fl} \approx \rho_{\text{gas}}$, and they produce a strong diffraction of light (opalescence). Also, in the collision of two heavy atomic nuclei there occur critical fluctuations in phase transitions. In that case, we deal with the phases of nuclear matter as, for example, pion condensates or the transition to a quark–gluon plasma. The critical fluctuations result in an increase of the nucleon cross sections, leading to distinct collective behavior (comparable to hydrodynamics).*

Let us now turn to the standard deviation of energy. The mean value is given by

$$\begin{aligned}\langle E\rangle &= \sum_{i,N} E_i p_{i,N} = \frac{1}{\mathcal{Z}} \sum_{i,N} E_i \exp\{-\beta\,(E_i - \mu N)\} \\ &= -\frac{1}{\mathcal{Z}}\,\frac{\partial}{\partial \beta}\,\mathcal{Z}\Big|_{z,V}\end{aligned} \tag{9.76}$$

In this differentiation the fugacity $z = \exp\{\beta\mu\}$ is kept constant, which is explicitly indicated by the index z in the derivation. The quantity $\langle E^2\rangle$ can be calculated similarly,

$$\begin{aligned}\langle E^2\rangle &= \sum_{i,N} E_i^2 p_{i,N} = \frac{1}{\mathcal{Z}}\,\frac{\partial^2}{\partial \beta^2}\,\mathcal{Z}\Big|_{z,V} \\ &= \frac{1}{\mathcal{Z}}\,\frac{\partial}{\partial \beta}\,(-\mathcal{Z}\,\langle E\rangle)\Big|_{z,V} = \langle E\rangle^2 - \left.\frac{\partial\,\langle E\rangle}{\partial \beta}\right|_{z,V}\end{aligned} \tag{9.77}$$

*cf. M. Gyulassy and W. Greiner *Annals of Physics* **109** (1977) 485.

so that

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = \left. \frac{\partial^2}{\partial \beta^2} \ln \mathcal{Z} \right|_{z,V} = - \left. \frac{\partial \langle E \rangle}{\partial \beta} \right|_{z,V} \tag{9.78}$$

If one inserts $\langle E \rangle = U$ into this equation, one obtains for the relative deviation from the mean energy

$$\frac{\sigma_E^2}{U^2} = \frac{kT^2}{U^2} \left(\frac{\partial U}{\partial T} \right)_{z,V} \tag{9.79}$$

This expression is not totally identical to Equation (7.124). There, instead of $\partial U/\partial T|_{z,V}$, we had the expression $\partial U/\partial T|_{N,V}$. However, the relation between both quantities follows from $U(T, V, N(T, V, z))$, where the particle number in the macrocanonical case depends on (T, V, μ) or on (T, V, z),

$$\left. \frac{\partial U}{\partial T} \right|_{z,V} = \left. \frac{\partial U}{\partial T} \right|_{V,N} + \left. \frac{\partial U}{\partial N} \right|_{T,V} \left. \frac{\partial N}{\partial T} \right|_{V,z} \tag{9.80}$$

Here $\partial U/\partial T|_{V,N} = C_V$ is the same expression as in Equation (7.124). Now we rewrite the last term in Equation (9.80). For $N(T, V, \mu)$ we have ($\mu = kT \ln z$),

$$\left. \frac{\partial N}{\partial T} \right|_{V,z} = \left. \frac{\partial N}{\partial T} \right|_{V,\mu} + \left. \frac{\partial N}{\partial \mu} \right|_{T,V} \left. \frac{\partial \mu}{\partial T} \right|_{V,z} \tag{9.81}$$

If one considers the complete differential of $N(T, V, \mu)$ for $V = \text{const.}$,

$$dN = \left. \frac{\partial N}{\partial T} \right|_{V,\mu} dT + \left. \frac{\partial N}{\partial \mu} \right|_{V,T} d\mu \tag{9.82}$$

then one has for $dN = 0$:

$$\left. \frac{\partial N}{\partial T} \right|_{V,\mu} = - \left. \frac{\partial N}{\partial \mu} \right|_{V,T} \left. \frac{\partial \mu}{\partial T} \right|_{N,V} \tag{9.83}$$

Observe that here the requirement $dN = 0$ enters on the right-hand side of Equation (9.82), since there occurs the term $\frac{\partial \mu}{\partial T}|_{N,V}$, i.e., the derivative at constant N, V, which had at first seemed arbitrary. Inserting this into Equation (9.81) yields, with $\partial \mu/\partial T|_{V,z} = \mu/T$,

$$\left. \frac{\partial N}{\partial T} \right|_{V,z} = \left. \frac{\partial N}{\partial \mu} \right|_{V,T} \left(\frac{\mu}{T} - \left. \frac{\partial \mu}{\partial T} \right|_{N,V} \right) \tag{9.84}$$

One more remark should be made concerning the relation $\frac{\partial \mu}{\partial T}|_{z,V} = \frac{\mu}{T}$. It follows by differentiation of $z = \exp\{\beta\mu\} = \text{const}$. This leads to $\mu(-\frac{1}{kT^2})z + \frac{1}{kT}\frac{\partial \mu}{\partial T}|_{z,V} z = 0$, which yields at once the asserted relation. Equation (9.84) can be simplified further. To this end, one considers $dU = T\,dS - p\,dV + \mu\,dN$:

$$\left. \frac{\partial U}{\partial N} \right|_{T,V} = \mu + T \left. \frac{\partial S}{\partial N} \right|_{T,V} = T \left(\frac{\mu}{T} - \left. \frac{\partial \mu}{\partial T} \right|_{N,V} \right) \tag{9.85}$$

In the last equation we have made use of the Maxwell relation (4.122), i.e., $-\frac{\partial S}{\partial N}|_{T,V} = \frac{\partial \mu}{\partial T}|_{V,N}$. Inserting this into Equations (9.84) and (9.80) leads to

$$\left.\frac{\partial U}{\partial T}\right|_{z,V} = C_V + \frac{1}{T}\left.\frac{\partial N}{\partial \mu}\right|_{V,T}\left(\left.\frac{\partial U}{\partial N}\right|_{T,V}\right)^2 \tag{9.86}$$

The relative fluctuation in energy is composed of two parts (consider Equation (9.68)):

$$\begin{aligned}\frac{\sigma_E^2}{U^2} &= \frac{kT^2}{U^2}C_V + \left(kT\left.\frac{\partial N}{\partial \mu}\right|_{V,T}\right)\left(\frac{1}{U}\left.\frac{\partial U}{\partial N}\right|_{T,V}\right)^2 \\ &= \frac{\sigma_{\text{can}}^2}{U^2} + \frac{\sigma_N^2}{U^2}\left(\left.\frac{\partial U}{\partial N}\right|_{T,V}\right)^2\end{aligned} \tag{9.87}$$

namely, the fluctuations which we had already in the canonical ensemble, plus fluctuations which are due to variations of particle number. The total fluctuation of energy in the macrocanonical case is larger than that in the canonical case, but it approaches zero like $O(1/\sqrt{N})$ for $N \to \infty$. *This is exactly the reason why all ensembles (microcanonical, canonical, and macrocanonical) for thermodynamic systems with large particle numbers yield the same result.*

We have already been able to show that one can calculate the density of state $g_N(E)$, which is closely related to the microcanonical quantity $\Omega(E, V, N)$, from the canonical partition function $Z(\beta, V, N)$ by an inverse Laplace transformation. Correspondingly, it is also possible to calculate the canonical partition function from the macrocanonical partition function $\mathcal{Z}$. To show this, it is best to start from Equation (9.40):

$$\mathcal{Z}(T, V, z) = \sum_{N=1}^{\infty} z^N Z(T, V, N) \tag{9.88}$$

Formally, in Equation (9.88) one can also allow for complex values of the variable $z = e^{\beta\mu}$. Then Equation (9.88) is nothing but the complex Taylor expansion of an analytic function $\mathcal{Z}(z)$. From function theory, however, it is well known how to determine the expansion coefficient $a_N = Z(T, V, N)$. There one has

$$Z(T, V, N) = \frac{1}{2\pi i}\oint_{\partial K}\frac{\mathcal{Z}(T, V, z)}{z^{N+1}}\,dz \tag{9.89}$$

Here one integrates on a sphere around the point $z = 0$ in the interior of the convergence radius of Equation (9.88). For noninteracting systems Equation (9.89) is trivial, since

$$\mathcal{Z}(T, V, z) = \exp\{zZ(T, V, 1)\} = \sum_{N=1}^{\infty}\frac{z^N}{N!}[Z(T, V, 1)]^N \tag{9.90}$$

leads to the well-known equation

$$Z(T, V, N) = \frac{1}{N!}[Z(T, V, 1)]^N \tag{9.91}$$

PART III

QUANTUM STATISTICS

10 Density Operators

Fundamentals

The starting point of classical statistical mechanics is the realization that a system can assume very many microstates for given macroscopic (thermodynamic) state quantities. In the framework of ensemble theory we were able to derive, with only a few, very general assumptions, the probability density of finding the system in a certain microstate. All observable quantities follow then as averages over all possible microstates with respect to this probability density. This concept is now to be transferred to quantum systems.

To this end, we have first to consider how to define a quantum mechanical microstate. In classical statistical mechanics, a microstate corresponds to a certain point in phase space $(\vec{r}_i, \vec{p}_i)$. For quantum mechanical systems, however, a simultaneous determination of the coordinates and momenta of the particles is not possible. The classical phase-space trajectory $(\vec{r}_i(t), \vec{p}_i(t))$ is replaced in quantum mechanics by the time evolution of the wavefunction $\Psi(\vec{r}_1, \ldots, \vec{r}_N, t)$ of the system. Let us for the moment again consider an isolated system with given macroscopic variables E, V, and N. The total wavefunction of the system is a solution of the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}_1, \ldots, \vec{r}_N, t) = \hat{H}\left(\vec{r}_i, \hat{\vec{p}}_i\right) \Psi(\vec{r}_1, \ldots, \vec{r}_N, t) \tag{10.1}$$

Since the total energy in an isolated system is also quantum mechanically a conserved quantity (for which reason $\hat{H}$ in Equation (10.1) does not explicitly depend on time), the time evolution of Equation (10.1) can be separated,

$$\Psi(\vec{r}_1, \ldots, \vec{r}_N, t) = \Psi_E(\vec{r}_1, \ldots, \vec{r}_N) \exp\left\{-i \frac{Et}{\hbar}\right\} \tag{10.2}$$

if the eigenfunction Ψ_E fulfills the stationary Schrödinger equation

$$\hat{H}\Psi_E(\vec{r}_1, \ldots, \vec{r}_N) = E\Psi_E(\vec{r}_1, \ldots, \vec{r}_N) \tag{10.3}$$

Since Equation (10.3) has, in general, solutions only for certain energy eigenvalues, the total energy E of the system can assume only certain values. For a system of macroscopic

dimensions, however, the energy eigenvalues are very near each other, and due to degeneracy many solutions may even exist for a certain energy E. We have already encountered an example of this in the microcanonical treatment of a system of N quantum mechanical particles in a box (cf. Chapter 5).

Furthermore, for macroscopic systems the exact determination of an energy is not at all realizable from a practical point of view. Therefore (as for the classical microcanonical ensemble), we allow again for a small energy uncertainty ΔE. Then there exist a lot of states having energy eigenvalues between E and $E + \Delta E$. This is, of course, all the more valid for systems with a continuous energy spectrum. *The specific microstates correspond to different wavefunctions* $\Psi_E^{(i)}(\vec{r}_1, \ldots, \vec{r}_N)$. One now obtains the microcanonical quantity $\Omega(E, V, N)$ simply by counting the states having energy eigenvalues between E and $E + \Delta E$, or for continuous spectra, by determining the *density of states* $g(E)$ and using $\Omega(E) = g(E)\Delta E$.

We proceed in exactly the same way as for the quantum mechanical microcanonical treatment of the ideal gas. Instead of averaging over all phase-space points of the energy shell $E \leq H(\vec{r}_i, \vec{p}_i) \leq E + \Delta E$, we have to average in the quantum mechanical case over all states $\Psi_E^{(i)}$ having an energy eigenvalue between E and $E + \Delta E$. However, a microstate $\Psi_E^{(i)}$ by no means yields a certain value for an arbitrary observable quantity $f(\vec{r}_i, \vec{p}_i)$; rather, f is measured with a certain probability.

In quantum mechanics, each observable $f(\vec{r}_i, \vec{p}_i)$ corresponds to a hermitean operator $\hat{f}(\hat{\vec{r}}_i, \hat{\vec{p}}_i)$. Such an operator has a set of eigenfunctions $\phi_f(\vec{r}_1, \ldots, \vec{r}_N)$, such that

$$\hat{f}\phi_f = f\phi_f \tag{10.4}$$

Each eigenvalue f corresponds to a possible measurable value of the observable quantity $f(\vec{r}_i, \vec{p}_i)$. In a microstate $\Psi_E^{(i)}$ one measures the eigenvalue f with the quantum mechanical probability amplitude

$$\left\langle \phi_f \middle| \Psi_E^{(i)} \right\rangle = \int d^3r_1 \cdots d^3r_N \phi_f^*(\vec{r}_1, \ldots, \vec{r}_N)\Psi_E^{(i)}(\vec{r}_1, \ldots, \vec{r}_N) \tag{10.5}$$

since $\Psi_E^{(i)}$ is just equal to the state ϕ_f with this probability amplitude (has the *overlap* (10.5) with ϕ_f). Thus, even for a certain microstate one obtains only a probability distribution for the possible measured values. If one performs measurements of the observable $f(\vec{r}_i, \vec{p}_i)$ in a set of identical systems in the same microstate $\Psi_E^{(i)}$, each eigenvalue f occurs with the probability amplitude $\left\langle \phi_f \middle| \Psi_E^{(i)} \right\rangle$. The quantum mechanical average of all measurements is the expectation value

$$\left\langle \Psi_E^{(i)} \middle| \hat{f} \middle| \Psi_E^{(i)} \right\rangle = \int d^3r_1 \cdots d^3r_N \Psi_E^{*(i)}(\vec{r}_1, \ldots, \vec{r}_N)\hat{f}(\hat{\vec{r}}_i, \hat{\vec{p}}_i)\Psi_E^{(i)}(\vec{r}_1, \ldots, \vec{r}_N) \tag{10.6}$$

In quantum statistics another average adds to this. One is no longer able to tell which specific microstate $\Psi_E^{(i)}$ the system assumes; one can give only a probability ρ_i of finding the wavefunction $\Psi_E^{(i)}$. If one now performs a measurement of the observable $\hat{f}$ in a set of such identical systems, one can measure only the average of the quantum mechanical

expectation values, weighted by the probabilities ρ_i,

$$\left\langle \hat{f} \right\rangle = \sum_i \rho_i \left\langle \Psi_E^{(i)} \left| \hat{f} \right| \Psi_E^{(i)} \right\rangle \tag{10.7}$$

This, however, is not the most general expression for the statistical average, since here we consider only diagonal expectation values $\left\langle \Psi_E^{(i)} \left| \hat{f} \right| \Psi_E^{(i)} \right\rangle$. In quantum mechanics there are also measurable quantities which depend on arbitrary matrix elements $\left\langle \Psi_E^{(i)} \left| \hat{f} \right| \Psi_E^{(k)} \right\rangle$, and one has to extend Equation (10.7):

$$\left\langle \hat{f} \right\rangle = \sum_{i,k} \rho_{ki} \left\langle \Psi_E^{(i)} \left| \hat{f} \right| \Psi_E^{(k)} \right\rangle \tag{10.8}$$

The quantity ρ_{ki} is now to be interpreted as the probability with which the matrix element $\left\langle \Psi_E^{(i)} \left| \hat{f} \right| \Psi_E^{(k)} \right\rangle$ contributes to the statistical average $\left\langle \hat{f} \right\rangle$ of the observable $\hat{f}$. The transition from the diagonal representation, Equation (10.7), to Equation (10.8) can be easily illustrated, if one expands the states $\Psi_E^{(i)}$ with respect to a complete set ϕ_k,

$$\Psi_E^{(i)} = \sum_k a_k^{(i)} \phi_k \tag{10.9}$$

If one inserts this into Equation (10.7), one obtains

$$\left\langle \hat{f} \right\rangle = \sum_i \rho_i \sum_{k,k'} a_k^{(i)*} a_{k'}^{(i)} \left\langle \phi_k \left| \hat{f} \right| \phi_{k'} \right\rangle = \sum_{k,k'} \left(\sum_i \rho_i a_k^{(i)*} a_{k'}^{(i)} \right) \left\langle \phi_k \left| \hat{f} \right| \phi_{k'} \right\rangle \tag{10.10}$$

The expression in brackets can now be identified with the more general probabilites $\rho_{k'k}$, which contain also nondiagonal terms,

$$\rho_{k'k} = \sum_i \rho_i a_{k'}^{(i)} a_k^{(i)*} \tag{10.11}$$

so that one obtains for Equation (10.10) the expression

$$\left\langle \hat{f} \right\rangle = \sum_{k,k'} \rho_{k'k} \left\langle \phi_k \left| \hat{f} \right| \phi_{k'} \right\rangle \tag{10.12}$$

One can now interpret the numbers $\rho_{k'k}$ as the matrix elements of an operator $\hat{\rho}$ in the basis of the ϕ_k, $\rho_{k'k} = \left\langle \phi_{k'} \left| \hat{\rho} \right| \phi_k \right\rangle$. Then Equation (10.12) reads

$$\left\langle \hat{f} \right\rangle = \sum_{k,k'} \left\langle \phi_{k'} \left| \hat{\rho} \right| \phi_k \right\rangle \left\langle \phi_k \left| \hat{f} \right| \phi_{k'} \right\rangle \tag{10.13}$$

or, because of the closure relation of the basis,

$$1 = \sum_k |\phi_k\rangle \langle \phi_k| \tag{10.14}$$

$$\left\langle \hat{f} \right\rangle = \sum_{k'} \left\langle \phi_{k'} \left| \hat{\rho} \hat{f} \right| \phi_{k'} \right\rangle = \mathrm{Tr}(\hat{\rho} \hat{f}) \tag{10.15}$$

As one observes, the statistical average of an observable $\hat{f}$ corresponds to the trace of the product of the operator $\hat{f}$ with a statistical operator $\hat{\rho}$, the *density operator*. The matrix elements ρ_{ki} in an arbitrary basis are just the probabilities with which the matrix elements $\left\langle i \left| \hat{f} \right| k \right\rangle$ of the observable $\hat{f}$ contribute to statistical averages in this basis (see Equation (10.12)).

From quantum mechanics one knows the general definition of the trace of an operator $\hat{O}$: $\mathrm{Tr}\,\hat{O} = \sum_k \langle \phi_k | \hat{O} | \phi_k \rangle$. The trace is just the sum of the expectation values of the operator (diagonal matrix elements) in an arbitrary basis. The value of the trace is independent of the basis chosen, since with $\phi_k = \sum_i S_{ki}\psi_i$ it follows immediately that

$$\sum_k \langle \phi_k | \hat{O} | \phi_k \rangle = \sum_{k,i,j} S_{ki}^* S_{kj} \langle \psi_i | \hat{O} \left| \psi_j \right\rangle$$

$$= \sum_{ij} \delta_{ij} \langle \psi_i | \hat{O} \left| \psi_j \right\rangle = \sum_i \langle \psi_i | \hat{O} | \psi_i \rangle \qquad \textbf{(10.16)}$$

The unitarity of the basis transformation $\hat{S}$ is required.

Expression (10.15) reduces, of course, to our initial Equation (10.7), if one uses the eigenstates of the operator $\hat{\rho}$ or of the observable $\hat{f}$ as a basis. In this basis, we either have $\rho_{ik} = \rho_i \delta_{ik}$ or $\left\langle i \left| \hat{f} \right| k \right\rangle = \left\langle i \left| \hat{f} \right| i \right\rangle \delta_{ik}$.

The prescription (10.15) for the calculation of statistical averages in quantum mechanics is exactly analogous to the classical statistical ensemble average,

$$\langle f(\vec{r}_i, \vec{p}_i) \rangle = \frac{1}{h^{3N}} \int d\omega \rho(\vec{r}_i, \vec{p}_i) f(\vec{r}_i, \vec{p}_i) \qquad \textbf{(10.17)}$$

the only difference being that in the quantum mechanical case one does not sum over all phase-space points $(\vec{r}_i, \vec{p}_i)$, but over all states which span the Hilbert space of the considered system. The density operator thus assumes the same role in quantum statistics as the phase-space density in classical statistical mechanics. The necessity of assigning an operator to the phase-space density in quantum mechanics becomes immediately clear, if one considers that the phase-space density itself is a classical observable, and we assign an operator to each classical observable in quantum mechanics,

$$\rho(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N, t) \rightarrow \hat{\rho}(\hat{\vec{r}}_1, \ldots, \hat{\vec{r}}_N, \hat{\vec{p}}_1, \ldots, \hat{\vec{p}}_N, t) \qquad \textbf{(10.18)}$$

In principle, we can now write down the density operators of the three classical ensembles; we have only to reinterpret the observables occurring in the classical phase-space density as operators.

However, before we do this, we want to investigate the difference between the statistical and the quantum mechanical average, as well as the general properties of the density operator, in more detail.

Pure and mixed states

If a quantum mechanical system is in a certain microstate, described by a state vector $|\Psi^{(i)}\rangle$, we say it is in a *pure state*. If on the other hand, the system can be in any of several different microstates $|\Psi^{(i)}\rangle$ with probabilities ρ_i, we are dealing with a *mixed state*. We now want to show that the mixed, as well as pure, states can be completely described by the matrix elements of the density operator; i.e., all quantum mechanical and statistical averages of arbitrary observables can be calculated if the density matrix is known.

To this end, we first denote the density operator in an arbitrary basis $|\phi_k\rangle$ in Dirac's notation,

$$\hat{\rho} = \sum_{k,k'} |\phi_{k'}\rangle \, \rho_{k'k} \, \langle\phi_k| \tag{10.19}$$

According to the preceding section, the diagonal matrix elements $\rho_{kk} = \langle\phi_k|\hat{\rho}|\phi_k\rangle$ are just the probabilities for the system to assume the special state $|\phi_k\rangle$, while the off-diagonal matrix elements $\rho_{k'k} = \langle\phi_{k'}|\hat{\rho}|\phi_k\rangle$ give the probabilities for the system to spontaneously make a transition from a state $|\phi_k\rangle$ to another state $|\phi_{k'}\rangle$. If we prepare our system in such a way that it may be in any of the states $|\Psi^{(i)}\rangle$ with the probabilities ρ_{ii}, and $\rho_{ik} = 0$ for $i \neq k$, the density operator is diagonal (states with sharply defined probability):

$$\hat{\rho} = \sum_i |\Psi^{(i)}\rangle \, \rho_{ii} \, \langle\Psi^{(i)}| \tag{10.20}$$

Here we assume that the states $|\Psi^{(i)}\rangle$ form an orthonormal system. The orthonormalization can always be achieved by Schmidt's procedure (see Volume 1). Pure states are defined by the fact that only one state vector contributes to the sum (10.20). For mixed states, several terms contribute; i.e., one cannot exactly determine the state that the system assumes. Note that the states $|\Psi^{(i)}\rangle$ are not necessarily complete in the full Hilbert space. They just span the subspace of the Hilbert space in which the state vector is not precisely determinable.

If several states $|\Psi(i)\rangle$ occur with the probability ρ_{ii}, the system is in a mixed state. However, it is in a pure state, if and only if the state vector $|\Psi^{(i)}\rangle$ of the system is precisely known; i.e., $\rho_{ii} = 1$ for one index i and zero otherwise. Thus Equation (10.20) becomes, for pure states,

$$\hat{\rho}^{\text{pure}} = |\Psi^{(i)}\rangle\langle\Psi^{(i)}| \tag{10.21}$$

If the system is in the precisely defined, pure state $|\Psi^{(i)}\rangle$, the density operator reduces to the projection operator

$$P_{|\Psi^{(i)}\rangle} = |\Psi^{(i)}\rangle\langle\Psi^{(i)}| \tag{10.22}$$

corresponding to this well-known state, and the respective subspace is one dimensional. The density matrix possesses only one nonvanishing element with respect to the states $|\Psi^{(i)}\rangle$, namely, $\rho_{ii} = 1$, and $\rho_{k'k} = 0$ otherwise. However, note that with respect to an arbitrary basis, the density matrix of a pure state may contain many matrix elements which

are different from zero. If one transforms Equation (10.21) to another basis, one finds

$$\hat{\rho}^{\text{pure}} = \sum_{kk'} |\phi_k\rangle \langle \phi_k | \Psi^{(i)}\rangle \langle \Psi^{(i)} | \phi_{k'}\rangle \langle \phi_{k'}| = \sum_{kk'} |\phi_k\rangle a_k^{(i)} a_{k'}^{(i)*} \langle \phi_{k'}| \tag{10.23}$$

if the $a_k^{(i)}$ are the expansion coefficients in Equation (10.9). With respect to this basis the density matrix reads

$$\rho_{kk'}^{\text{pure}} = a_k^{(i)} a_{k'}^{(i)*} \tag{10.24}$$

From the general properties of projection operators,

$$P_{|\Psi\rangle}^2 = P_{|\Psi\rangle} \tag{10.25}$$

since $|\Psi\rangle \langle \Psi| \Psi\rangle \langle \Psi| = |\Psi\rangle \langle \Psi|$, a convenient criterion follows for the case when the density matrix describes a pure state. In this case it must be valid—independent of the basis—that

$$(\hat{\rho}^{\text{pure}})^2 = \hat{\rho}^{\text{pure}} \tag{10.26}$$

If, on the other hand, the system may assume several (or even infinitely many) states $|\Psi^{(i)}\rangle$ with the definite probabilities ρ_{ii}, the state vector is not fixed, but every vector of the subspace spanned by the $|\Psi^{(i)}\rangle$ may contribute. The ρ_{ii} are then the probabilities of finding the special component $|\Psi^{(i)}\rangle$ in the mixed state. To be able to interpret them as probabilities, it must of course hold that

$$\sum_i \rho_{ii} = 1$$

$$0 \leq \rho_{ii} \leq 1 \tag{10.27}$$

We now want to show that if the density matrix is known in one basis, all quantum mechanical observables can be calculated. Let $\hat{f}$ be an observable of the system and $|\phi_f\rangle$ be the eigenstates corresponding to the eigenvalue f. The most general measurable quantity is the probability $|\langle \phi_f | \Psi^{(i)}\rangle|^2$, of measuring the eigenvalue f in the pure state $|\Psi^{(i)}\rangle$. This probability can be also expressed by the density matrix $\hat{\rho}^{\text{pure}} = |\Psi^{(i)}\rangle \langle \Psi^{(i)}|$ belonging to the pure state $|\Psi^{(i)}\rangle$. Let $P_{|\phi^{(f)}\rangle} = |\phi_f\rangle \langle \phi_f|$ be the projection onto the eigenstate of the observable $\hat{f}$ belonging to the eigenvalue f (just as $\hat{\rho}^{\text{pure}}$ is the projection onto the state $|\Psi^{(i)}\rangle$). Then the following identity holds:

$$|\langle \phi_f | \Psi^{(i)}\rangle|^2 = \text{Tr}(\hat{\rho}^{\text{pure}} P_{|\phi^{(f)}\rangle}) \tag{10.28}$$

To prove this identity, we have to recalculate the trace in Equation (10.28) in terms of the basis of eigenstates $|\phi_f\rangle$ of the operator $\hat{f}$. It is

$$\begin{aligned} \text{Tr}(\hat{\rho}^{\text{pure}} P_{|\phi^{(f)}\rangle}) &= \sum_{f'} \langle \phi_{f'} | \hat{\rho}^{\text{pure}} \hat{P}_{|\phi_f\rangle} | \phi_{f'}\rangle \\ &= \sum_{f'} \langle \phi_{f'} | \Psi^{(i)}\rangle \langle \Psi^{(i)} | \phi_f\rangle \langle \phi_f | \phi_{f'}\rangle \\ &= \langle \phi_f | \Psi^{(i)}\rangle \langle \Psi^{(i)} | \phi_f\rangle \end{aligned} \tag{10.29}$$

Here the expressions for $\hat{\rho}^{\text{pure}} = |\Psi^{(i)}\rangle\langle\Psi^{(i)}|$ and $P_{|\phi_f\rangle} = |\phi_f\rangle\langle\phi_f|$ were explicitly inserted, and the orthogonality of the basis, $\langle\phi_f|\phi_{f'}\rangle = \delta_{ff'}$, was exploited. Due to the factor $\delta_{ff'}$ the sum reduces to the term with $f = f'$. Quite analogously, we obtain in a mixed state

$$\begin{aligned}\text{Tr}\left(\hat{\rho}P_{|\phi_f\rangle}\right) &= \sum_{f'}\sum_{i}\langle\phi_{f'}|\Psi^{(i)}\rangle\rho_{ii}\langle\Psi^{(i)}|\phi_f\rangle\langle\phi_f|\phi_{f'}\rangle \\ &= \sum_{i}\langle\phi_f|\Psi^{(i)}\rangle\rho_{ii}\langle\Psi^{(i)}|\phi_f\rangle \\ &= \sum_{i}\rho_{ii}\left|\langle\phi_f|\Psi^{(i)}\rangle\right|^2 \end{aligned} \tag{10.30}$$

i.e., the superposition of the quantum mechanical probabilities $\left|\langle\phi_f|\Psi^{(i)}\rangle\right|^2$ for each state $|\Psi^{(i)}\rangle$ with the statistical probabilities ρ_{ii}.

In general, performing the trace for an arbitrary operator and an arbitrary basis $|\Phi_k\rangle$ yields

$$\begin{aligned}\langle\hat{f}\rangle = \text{Tr}\left(\hat{\rho}\hat{f}\right) &= \sum_{ki}\langle\Phi_k|\Psi^{(i)}\rangle\rho_{ii}\langle\Psi^{(i)}|\hat{f}|\Phi_k\rangle \\ &= \sum_{i}\rho_{ii}\sum_{kk'}\langle\Phi_k|\Psi^{(i)}\rangle\langle\Psi^{(i)}|\Phi_{k'}\rangle\langle\Phi_{k'}|\hat{f}|\Phi_k\rangle \\ &= \sum_{i}\rho_{ii}\sum_{kk'}a_k^{(i)}a_{k'}^{(i)*}\langle\Phi_{k'}|\hat{f}|\Phi_k\rangle \end{aligned} \tag{10.31}$$

which, of course, agrees with Equations (10.10), (10.12) and (10.18). In Equation (10.31), however, one readily observes the main difference between the quantum mechanical average, with amplitudes $a_k^{(i)}$, and the statistical average, with probabilities ρ_{ii}. The amplitudes $a_k^{(i)}$ are complex numbers having absolute values and phases, while the ρ_{ii} are real number probabilities. This means that in the quantum mechanical average, interferences may occur—to speak in the language of the wave picture—but this is not the case for the statistical average.

Let us, for instance, consider the subspace spanned by the vectors $|\Psi^{(i)}\rangle$. If the state vector $|\Psi\rangle$ of the system is exactly known, a linear combination

$$|\Psi\rangle = \sum_{i}a_i|\Psi^{(i)}\rangle \tag{10.32}$$

can be formed, where the $|\Psi^{(i)}\rangle$ have, perhaps, to be made into a completed orthonormal system by adding further vectors. The coefficients $a_i = \langle\Psi^{(i)}|\Psi\rangle$ are complex numbers with certain absolute values and relative phases (the absolute phase of the wavefunction is, as one knows, irrelevant). The quantum mechanical expectation value of an observable $\hat{f}$ now reads

$$\langle\Psi|\hat{f}|\Psi\rangle = \sum_{i,k}a_i^*a_k\langle\Psi^{(i)}|\hat{f}|\Psi^{(k)}\rangle \tag{10.33}$$

However, if one forms the purely statistical average in a mixed state, where the $|\Psi^{(i)}\rangle$ just appear with the probabilities ρ_{ii},

$$\langle \hat{f} \rangle = \sum_i \rho_{ii} \langle \Psi^{(i)} | \hat{f} | \Psi^{(i)} \rangle \tag{10.34}$$

One observes that the mixed terms drop out in the latter case. Even if one prepares a system in such a way that in the mixed state the ρ_{ii} correspond by their numbers exactly to the $|a_i|^2$, nevertheless in general one does not obtain the same average, since information about the phases is not contained in the statistical average.

The quantum mechanical average (10.33) is called *coherent* due to the possibility of interference, while the statistical average (10.34) is called *incoherent.*

Example 10.1: The free electron

A free electron with spin can be described by the wavefunction

$$\Phi_{\vec{k},s}(\vec{r}) = \frac{1}{(2\pi)^{3/2}} \exp\left\{ i\vec{k} \cdot \vec{r} \right\} \chi_s$$

with

$$\chi_{+1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\chi_{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

where $s = \pm 1/2$ characterizes the two possible spin projections. Each linear combination

$$\Psi_{\vec{k}} = a_+ \Phi_{\vec{k},+1/2} + a_- \Phi_{\vec{k},-1/2} \tag{10.35}$$

is an eigenfunction of the free Hamiltonian. The two functions $\Phi_{\vec{k},+1/2}$ and $\Phi_{\vec{k},-1/2}$ are orthonormalized, and thus span a subspace of Hilbert space for each momentum or energy eigenvalue. According to Equation (10.35), in the state $\Psi_{\vec{k}}$ one measures the spin projections $s = \pm 1/2$ with the probabilities $|a_\pm|^2$.

As one knows, a certain spin projection of the electron corresponds to a polarized electron wave. For instance, for $a_+ = 1$ and $a_- = 0$ the wave is right-handed polarized and for $a_+ = 0$ and $a_- = 1$ it is left-handed polarized. But according to Equation (10.35), all coherent linear combinations correspond to a definite polarization state, in general to elliptical polarization. One can describe the polarization by the polarization vector

$$\vec{P} = \langle \Psi_{\vec{k}} | \vec{\sigma} | \Psi_{\vec{k}} \rangle,$$

where the $\vec{\sigma}$ are the Pauli matrices. If we insert Equation (10.35) and use the orthonormality of plane waves, we obtain

$$\vec{P} = (a_+^*, a_-^*)\, \vec{\sigma} \begin{pmatrix} a_+ \\ a_- \end{pmatrix} = \begin{pmatrix} a_+^* a_- + a_-^* a_+ \\ i\,(a_-^* a_+ - a_+^* a_-) \\ a_+^* a_+ - a_-^* a_- \end{pmatrix}$$

Because $|a_+|^2 + |a_-|^2 = 1$, one readily convinces oneself that always $|\vec{P}| = 1$; i.e., the system is maximally polarized. However, if one measures the polarization in a statistical ensemble of electrons (e.g., from a hot cathode), these electrons have in general no polarization at all. This, however, does not simply mean that both spin projections $s = \pm 1/2$ in an unpolarized electron beam occur equally often (this would also be the case in a linearly polarized electron beam with $|a_+| = |a_-| = 1/\sqrt{2}$), but that in the statistical ensemble the state vector in the subspace corresponding to $s = \pm 1/2$ is not determined. One can give only real probabilities ρ_+ and ρ_- of finding an electron in the states $\Phi_{\vec{k},+1/2}$ or $\Phi_{\vec{k},-1/2}$, which means that all relative phases of both states may occur. The corresponding polarization vector follows from incoherent (statistical) averaging:

$$\left\langle \vec{P} \right\rangle = \rho_+ \left\langle \Phi_{\vec{k},+1/2} \left| \vec{\sigma} \right| \Phi_{\vec{k},+1/2} \right\rangle + \rho_- \left\langle \Phi_{\vec{k},-1/2} \left| \vec{\sigma} \right| \Phi_{\vec{k},-1/2} \right\rangle$$

$$= \rho_+ \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} + \rho_- \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \rho_+ - \rho_- \end{pmatrix}$$

If both probabilities are $\rho_+ = \rho_- = 1/2$, the beam is completely unpolarized $\left|\left\langle \vec{P} \right\rangle\right| = 0$.

In this example, it becomes clear that we deal with a mixed state if we do not have the maximum information which it is possible to obtain by quantum mechanics, i.e., if one determines only a few quantum numbers (in this example, the energy) from a lot of numbers (energy, spin projection, etc.).

Now several quantum numbers in one state always correspond to several mutually commuting operators, which can be simultaneously cast into diagonal form. The subspace of the Hilbert space, in which the state vector is not fixed, is now spanned by just that eigenstates of the operators, whose quantum numbers are not determined. In particular, the density matrix is diagonal with respect to this basis. For instance, the density matrix in the preceding example of electrons with spin reads

$$\rho_{s,s'} = \begin{pmatrix} \rho_+ & 0 \\ 0 & \rho_- \end{pmatrix} \qquad \rho_+ + \rho_- = 1 \tag{10.36}$$

On the other hand, the density matrix of the pure state (10.35) can be expressed by the $a_\pm$, or even simpler, by the polarization vector,

$$\rho_{s,s'}^{\text{pure}} = \begin{pmatrix} a_+ \\ a_- \end{pmatrix} (a_+^* a_-^*) = \begin{pmatrix} a_+^* a_+ & a_-^* a_+ \\ a_+^* a_- & a_-^* a_- \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 + P_z & P_x - iP_y \\ P_x + iP_y & 1 - P_z \end{pmatrix} \tag{10.37}$$

Properties of the density matrix

Some important properties fulfilled by the density matrix can be directly extracted from the two preceding sections. From the definition of the matrix elements of the density matrix in an arbitrary basis,

$$\rho_{kk'} = \sum_i \rho_i a_{k'}^{(i)} a_k^{(i)*} \tag{10.38}$$

the hermiticity of the density matrix immediately follows,

$$\rho_{k'k}^* = \rho_{kk'} \qquad \text{or} \qquad \hat{\rho}^+ = \hat{\rho} \tag{10.39}$$

since the ρ_i are real. From the normalization, $\sum_i \rho_i = 1$, one concludes that

$$\sum_k \rho_{kk} = \sum_i \rho_i \left(\sum_k \left| a_k^{(i)} \right|^2 \right) = 1 \qquad \text{or} \qquad \operatorname{Tr} \hat{\rho} = 1 \tag{10.40}$$

The density matrix represents a pure state if, as already mentioned,

$$\hat{\rho}^2 = \hat{\rho} \tag{10.41}$$

The matrix elements

$$\rho_{k'k} = \langle \Phi_{k'} | \hat{\rho} | \Phi_k \rangle \tag{10.42}$$

in an arbitrary basis are to be interpreted as the probabilities that the system assumes the state $|\Phi_k\rangle$ (probability ρ_{kk}), or makes a spontaneous transition from the state $|\Phi_k\rangle$ to the state $|\Phi_{k'}\rangle$, respectively. Accordingly, the density matrix of a particle in coordinate space representation,

$$\rho(\vec{r}', \vec{r}) = \langle \vec{r}' | \hat{\rho} | \vec{r} \rangle \tag{10.43}$$

is to be interpreted as the transition probability of the particle to go from $\vec{r}$ to $\vec{r}'$. The diagonal elements $\rho(\vec{r}) = \langle \vec{r} | \hat{\rho} | \vec{r} \rangle$ especially are just the density distribution in coordinate space. Analogously, the momentum distribution follows via the diagonal elements from the representation of the density matrix in momentum space, $\langle \vec{p}' | \hat{\rho} | \vec{p} \rangle$. Note that one obtains only the coordinate space distribution or the momentum distribution, but not both simultaneously, in accordance with the uncertainty relation. However, the density matrix contains, in addition, information which cannot be understood from a classical point of view. For instance, the spontaneous transition probability of a particle from point $\vec{r}$ to point $\vec{r}'$, measured through $\langle \vec{r}' | \hat{\rho} | \vec{r} \rangle$, has no classical analogy.

Let us now study the time evolution of the density matrix. To this end, we allow for a temporal change of the particular states $|\Psi^{(i)}(t)\rangle$ (in the Schrödinger picture), over which one has to average, with the probabilities ρ_i. Each of the state vectors fulfills the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi^{(i)}(t)\rangle = \hat{H} |\Psi^{(i)}(t)\rangle \tag{10.44}$$

or its hermitian conjugate

$$-i\hbar \frac{\partial}{\partial t} \left\langle \Psi^{(i)}(t) \right| = \left\langle \Psi^{(i)}(t) \right| \hat{H} \tag{10.45}$$

On the other hand, the probabilities ρ_i do not change with time,

$$\frac{d}{dt} \rho_i = 0 \tag{10.46}$$

They merely determine how accurately we fixed the state vector in the beginning ($t = 0$). Afterwards, however, the system may evolve according to its Hamiltonian, and the ρ_i will stay constant, as long as one does not interfere from outside. We obtain the time dependence of the density matrix via

$$\begin{aligned} i\hbar \frac{d}{dt} \hat{\rho} &= i\hbar \frac{d}{dt} \sum_i \left| \Psi^{(i)}(t) \right\rangle \rho_i \left\langle \Psi^{(i)}(t) \right| \\ &= \sum_i \left\{ \hat{H} \left| \Psi^{(i)}(t) \right\rangle \rho_i \left\langle \Psi^{(i)}(t) \right| - \left| \Psi^{(i)}(t) \right\rangle \rho_i \left\langle \Psi^{(i)}(t) \right| \hat{H} \right\} \\ &= \hat{H}\hat{\rho} - \hat{\rho}\hat{H} \end{aligned} \tag{10.47}$$

or

$$i\hbar \frac{d}{dt} \hat{\rho} = \left[\hat{H}, \hat{\rho} \right] \tag{10.48}$$

This equation of motion of the density matrix is named after *von Neumann*. It is the analogy to the Liouville equation for the classical phase-space density:

$$\frac{d\rho(\vec{r}_i, \vec{p}_i, t)}{dt} = \frac{\partial}{\partial t} \rho(\vec{r}_i, \vec{p}_i, t) + \{H, \rho\} = 0 \tag{10.49}$$

Note that in quantum mechanics the classical *Poisson bracket* $\{H, \rho\}$ is transformed into the commutator $1/i\hbar \left[\hat{H}, \hat{\rho} \right]$. Let us emphasize that von Neumann's equation (10.48) must not be confused with the dynamics of operators in the Heisenberg picture. This is given by

$$i\hbar \frac{d}{dt} \hat{O}_H \left(\hat{q}(t), \hat{p}(t), t \right) = i\hbar \frac{\partial}{\partial t} \hat{O}_H \left(\hat{q}, \hat{p}, t \right) + \left[\hat{O}_H, \hat{H}_H \right] \tag{10.50}$$

where all states $\left| \Psi^{(i)} \right\rangle$ in the Heisenberg picture remain time-independent. Since the density matrix is just a linear combination of projectors onto these time-independent state vectors, in the Heisenberg picture it holds that

$$\frac{d}{dt} \hat{\rho}_H = 0 \tag{10.51}$$

In contrast, von Neumann's equation refers to the Schrödinger picture, where the operators possess only an explicit time dependence, but where the state vectors $\left| \Psi^{(i)}(t) \right\rangle$ are time-dependent. For the dependence on time of the expectation value of an arbitrary operator $\hat{f}$

one obtains (Schrödinger picture)

$$i\hbar \frac{d}{dt}\left\langle \hat{f} \right\rangle = i\hbar \frac{d}{dt} \operatorname{Tr}\left(\hat{\rho}\hat{f}\right) = \operatorname{Tr}\left(i\hbar \frac{d}{dt}\left(\hat{\rho}\hat{f}\right)\right)$$

$$= \operatorname{Tr}\left(\left[\hat{H}, \hat{\rho}\right]\hat{f} + \hat{\rho}\left(i\hbar \frac{\partial \hat{f}}{\partial t}\right)\right)$$

$$= \operatorname{Tr}\left(\left[\hat{H}, \hat{\rho}\right]\hat{f}\right) + i\hbar\left\langle \frac{\partial \hat{f}}{\partial t} \right\rangle \tag{10.52}$$

where $\hat{f}$ can at most depend explicitly on time in the Schrödinger picture. A density operator, which fulfills

$$i\hbar \frac{d}{dt}\hat{\rho} = \left[\hat{H}, \hat{\rho}\right] = 0 \tag{10.53}$$

is called *stationary*. In this case, which is completely analogous to the classical stationary ensemble, one does not obtain any contribution from the time dependence of the density operator to the time dependence of the expectation values.

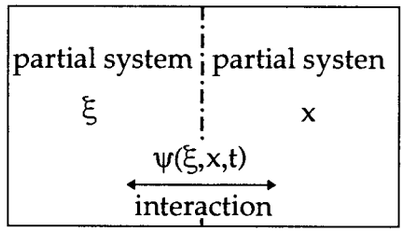


Figure 10.1. System consisting of two interacting partial systems.

We now want to consider the density matrix once again, but from another point of view. Let a total system be given which consists of two interacting partial systems (Figure 10.1). To the first partial system we assign the coordinates ξ, to the second the coordinates x. The time evolution of the total wavefunction $\Psi(\xi, x, t)$ is determined by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\Psi(\xi, x, t) = \hat{H}(\xi, x)\Psi(\xi, x, t) \tag{10.54}$$

Let $\hat{S}(x)$ be an observable with the complete set of eigenfunctions $\phi_S(x)$, which depend only on the coordinates x of one partial system. Then the total wavefunction can be expanded in terms of the $\phi_S(x)$, where the expansion coefficients $\Phi_S(\xi, t)$ depend on the ξ and on t. Wavefunctions of the system with the coordinates ξ are

$$\Psi(\xi, x, t) = \sum_S \Phi_S(\xi, t)\phi_S(x) \tag{10.55}$$

Furthermore, let $\hat{f}(x)$ be any other observable of the partial system corresponding to x. Then the expectation value is

$$\left\langle \Psi \left| \hat{f} \right| \Psi \right\rangle = \sum_{S,S'} \left\langle \Phi_S(\xi, t)\phi_S(x) \left| \hat{f}(x) \right| \Phi_{S'}(\xi, t)\phi_{S'}(x) \right\rangle$$

$$= \sum_{S,S'} \langle \Phi_S(\xi, t) | \Phi_{S'}(\xi, t) \rangle \left\langle \phi_S(x) \left| \hat{f}(x) \right| \phi_{S'}(x) \right\rangle \tag{10.56}$$

Here two space integrations (Dirac brackets) appear, since one has to integrate over x as well as over ξ in the expectation value $\left\langle \Psi \left| \hat{f} \right| \Psi \right\rangle$. If we now set

$$\rho_{S',S}(t) = \langle \Phi_S(\xi, t) | \Phi_{S'}(\xi, t) \rangle \tag{10.57}$$

Equation (10.56) becomes

$$\left\langle \Psi \left| \hat{f} \right| \Psi \right\rangle = \sum_{S,S'} \rho_{S',S} \left\langle \phi_S(x) \left| \hat{f}(x) \right| \phi_{S'}(x) \right\rangle = \mathrm{Tr}\left(\hat{\rho}\hat{f}\right) \tag{10.58}$$

Obviously Equation (10.57) defines a density matrix for the partial system x. The density matrix thus describes the external influence of the partial systems on the system in which the observable $\hat{f}(x)$ is observed. In practice, the partial system with the coordinates ξ may be, for instance, a heat bath or something similar.

It is interesting to calculate once again the time dependence of the density matrix, using Equation (10.57)

$$i\hbar \dot{\rho}_{S'S}(t) = i\hbar \int d\xi \left\{ \dot{\Phi}^*_S(\xi, t)\Phi_{S'}(\xi, t) + \Phi^*_S(\xi, t)\dot{\Phi}_{S'}(\xi, t) \right\} \tag{10.59}$$

One obtains the two time derivatives by inserting Equation (10.55) in (10.54), multiplying by $\phi^*_{S'}(x)$, and integrating over x:

$$i\hbar \frac{\partial}{\partial t} \Phi_{S'}(\xi, t) = \sum_K \left\langle \phi_{S'}(x) \left| \hat{H}(\xi, x) \right| \phi_K(x) \right\rangle \Phi_K(\xi, t) \tag{10.60}$$

The matrix element still depends on the coordinates ξ; let us denote it by $H_{S'K}(\xi)$. Then we obtain

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Phi_{S'}(\xi, t) &= \sum_K H_{S'K}(\xi)\Phi_K(\xi, t) \\ i\hbar \frac{\partial}{\partial t} \Phi^*_S(\xi, t) &= -\sum_K \Phi^*_K(\xi, t)H_{KS}(\xi) \end{aligned} \tag{10.61}$$

If one inserts this into Equation (10.59), one gets

$$i\hbar \dot{\rho}_{S'S}(t) = \sum_K \int d\xi \left\{ \Phi^*_S(\xi, t)H_{S'K}(\xi)\Phi_K(\xi, t) - \Phi^*_K(\xi, t)H_{KS}(\xi)\Phi_{S'}(\xi, t) \right\} \tag{10.62}$$

Here, one cannot in general express the right-hand side in terms of the density matrix (10.57), except for the case where the Hamiltonian $\hat{H}(\xi, x)$ actually does not depend on ξ. Then the $H_{S'K}(\xi) = H_{S'K}$ are mere numbers and can be brought in front of the integral. Then, and only then, the integrals over $\Phi^*_S\Phi_K$ and $\Phi^*_K\Phi_{S'}$ can be expressed again in terms of ρ_{KS} and $\rho_{S'K}$ according to Equation (10.57). In this case Equation (10.62) reduces to

$$i\hbar \dot{\rho}_{S'S}(t) = \sum_K \{H_{S'K}\rho_{KS} - \rho_{S'K}H_{KS}\} \tag{10.63}$$

i.e., just to von Neumann's equation. *Thus, a necessary condition for the validity of von Neumann's equation is that the system does not interact with its surroundings*; i.e., the

Hamiltonian of the partial system $\hat{H}(x)$ must not depend on the external coordinates. This is in complete agreement with our prior assertion that the probabilities ρ_i are time-independent as long as one does not interfere from outside.

The density operators of quantum statistics

After these preliminaries, it is not difficult to rewrite the classical phase-space densities in terms of density operators. These can depend only on conserved quantities, since according to the preceding section, for stationary ensembles it must be valid that $\left[\hat{H}, \hat{\rho}\right] = 0$. Since the classical phase-space densities depend essentially on the Hamiltonian, it is convenient to use energy eigenstates as a basis, which are defined by

$$\hat{H} \left|\phi_n\right\rangle = E_n \left|\phi_n\right\rangle \tag{10.64}$$

where the index n enumerates all different states. In this basis the density operators have to be diagonal,

$$\rho_{mn} = \rho_n \delta_{mn} \tag{10.65}$$

The quantities $\rho_n = \left\langle \phi_n \left| \hat{\rho} \right| \phi_n \right\rangle$ can be interpreted as the probabilities that a system assumes the special energy states $\left|\phi_n\right\rangle$. Thus, if one measures the energy state in a large number of identical systems (an ensemble) which have the same Hamiltonian and the same density matrix, one will find an arbitrarily chosen system in the energy state E_n with probability ρ_n. In the microcanonical ensemble we fix the energy E of an isolated system up to a small uncertainty ΔE. All states with an energy between E and $E + \Delta E$ have equal probability. This is a consequence of our fundamental assumption of equal elementary probability of the microstates. It holds in the *microcanonical case* that

$$\rho_n = \begin{cases} 1/\Omega & E \leq E_n \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{10.66}$$

if $\Omega(E, V, N)$ is the number of states in the considered energy interval. In a system with a continuous energy spectrum, one first calculates the density of states $g(E)$, and then $\Omega = g\Delta E$.

Note that the probabilities ρ_n can be derived in the same manner as in the classical case. Now the discrete energy states E_n assume the role of the surface elements on the energy surface. One can denote the density operator also in general in an arbitrary basis. To this end, we start from Equation (6.3), and interpret the classical Hamiltonian as operator

$$\hat{\rho} = \frac{\delta\left(\hat{H} - E \cdot 1\right)}{\mathrm{Tr}\left(\delta\left(\hat{H} - E \cdot 1\right)\right)} \tag{10.67}$$

This expression looks somewhat pathological, and is not very well suited for calculation. In practice, one does better to use the simpler energy representation (10.66). The denominator

in Equation (10.67) effects the normalization $\mathrm{Tr}\,\hat{\rho} = 1$, while the δ-function vanishes, as long as $\hat{\rho}$ does not act on a state with the energy eigenvalue E.

The *canonical density operator* has in the energy representation the diagonal matrix elements

$$\rho_n = \frac{\exp\{-\beta E_n\}}{\sum_n \exp\{-\beta E_n\}} \tag{10.68}$$

with the partition function

$$Z(T, V, N) = \sum_n \exp\{-\beta E_n\} \tag{10.69}$$

Also, in this case, the operator can be written generally in an arbitrary basis,

$$\hat{\rho} = \frac{\exp\left\{-\beta \hat{H}\right\}}{\mathrm{Tr}\left(\exp\left\{-\beta \hat{H}\right\}\right)} \tag{10.70}$$

The exponential function of the operator is to be interpreted as a Taylor series expansion:

$$\exp\left\{-\beta \hat{H}\right\} = \sum_{k=0}^{\infty} \frac{\left(-\beta \hat{H}\right)^k}{k!} \tag{10.71}$$

The trace in the denominator of Equation (10.70) again effects the normalization and is identical with the partition function,

$$\begin{aligned} \mathrm{Tr}\left(\exp\left\{-\beta \hat{H}\right\}\right) &= \sum_n \left\langle \phi_n \left| \exp\left\{-\beta \hat{H}\right\} \right| \phi_n \right\rangle \\ &= \sum_n \langle \phi_n \,|\exp\{-\beta E_n\}|\, \phi_n \rangle \\ &= \sum_n \exp\{-\beta E_n\} = Z(T, V, N) \end{aligned} \tag{10.72}$$

Here, we used the fact that the $|\phi_n\rangle$ are eigenstates of $\hat{H}$ with the eigenvalue E_n, so that one simply obtains $\exp\{-\beta E_n\}$ by applying $\exp\left\{-\beta \hat{H}\right\}$ on an energy eigenstate.

From the knowledge of the density matrix in any representation, one can determine all observable quantities of the system. For instance, the average of an observable $\left\langle \hat{f} \right\rangle$ is given by

$$\left\langle \hat{f} \right\rangle = \mathrm{Tr}\left(\hat{\rho} \hat{f}\right) = \frac{\mathrm{Tr}\left(\exp\left\{-\beta \hat{H}\right\} \hat{f}\right)}{\mathrm{Tr}\left(\exp\left\{-\beta \hat{H}\right\}\right)} \tag{10.73}$$

This prescription is quite analogous to the classical ensemble average. There we had, instead of the trace (sum over all states), the respective phase-space integral (cf., for instance

Equation (7.69)). Especially for the mean energy, one has

$$U = \left\langle \hat{H} \right\rangle = \frac{\mathrm{Tr}\left(\exp\left\{-\beta\hat{H}\right\}\hat{H}\right)}{\mathrm{Tr}\left(\exp\left\{-\beta\hat{H}\right\}\right)} = -\frac{\partial}{\partial\beta}\ln\left(\mathrm{Tr}\exp\left\{-\beta\hat{H}\right\}\right) \tag{10.74}$$

or

$$U = -\frac{\partial}{\partial\beta}\ln Z(T, V, N) \tag{10.75}$$

From the partition function $Z(T, V, N)$ we thus obtain, exactly as in the classical case, all thermodynamic observables from derivatives (cf., (7.87)ff). Of course, we identify the entropy with the average

$$S = \left\langle -k\ln\hat{\rho}\right\rangle = -k\,\mathrm{Tr}\left(\hat{\rho}\ln\hat{\rho}\right) \tag{10.76}$$

where the operator *logarithm* is formally simply the inverse of the exponential function. Especially for the canonical density operator, one obtains with Equation (10.70):

$$S = -k\,\mathrm{Tr}\left(\hat{\rho}\left(-\beta\hat{H} - \ln Z(T, V, N)\right)\right) = k\beta\left\langle\hat{H}\right\rangle + k\ln Z(T, V, N) \tag{10.77}$$

from which immediately follows, with Equation (10.74) and $\beta = 1/kT$,

$$F = U - TS = -kT\ln Z(T, V, N) = -kT\ln\left\{\mathrm{Tr}\left(\exp\left\{-\beta\hat{H}\right\}\right)\right\} \tag{10.78}$$

The equations remain the same as in the classical case, but now one has to calculate the partition function using Equations (10.69) or (10.70).

For the *grand canonical density operator* the diagonal matrix elements read, in the energy representation,

$$\rho_n = \frac{\exp\{-\beta(E_n - \mu N)\}}{\sum_{n,N}\exp\{-\beta(E_n - \mu N)\}} \tag{10.79}$$

The *grand canonical partition function* becomes

$$\mathcal{Z}(T, V, \mu) = \sum_{n,N}\exp\{-\beta(E_n - \mu N)\} = \sum_{N=0}^{\infty} z^N Z(T, V, N) \tag{10.80}$$

As in the classical case, it can be expressed as a sum over all canonical partition functions with different particle numbers N, weighted by the fugacity $z = \exp\{\beta\mu\}$. In operator notation, Equation (10.79) becomes

$$\hat{\rho} = \frac{\exp\left\{-\beta\left(\hat{H} - \mu\hat{N}\right)\right\}}{\mathrm{Tr}\left(\exp\left\{-\beta\left(\hat{H} - \mu\hat{N}\right)\right\}\right)} \tag{10.81}$$

Here one has to consider that in quantum mechanics the particle number N is an operator, $\hat{N}$. Only for systems with fixed particle number can the operator be replaced by the eigenvalue N. For systems where the creation and annihilation of particles happens, the operator $\hat{\rho}$ acts in a generalized Hilbert space, the so-called *Fock space*. This space is the direct sum of all

Hilbert spaces with fixed particle number. Correspondingly, the trace in the denominator of Equation (10.81) runs over the matrix elements of $\exp\left\{-\beta\left(\hat{H}-\mu\hat{N}\right)\right\}$, calculated with states of the Fock space. For the entropy it follows that

$$S = \langle -k \ln \hat{\rho} \rangle = -k \operatorname{Tr}\left(\hat{\rho}\left(-\beta\hat{H} + \beta\mu\hat{N} - \ln \mathcal{Z}(T, V, \mu)\right)\right)$$

$$= k\beta\left\langle\hat{H}\right\rangle - k\beta\mu\left\langle\hat{N}\right\rangle + k \ln \mathcal{Z} \tag{10.82}$$

This can be expressed again in terms of thermodynamic quantities,

$$\Phi = U - TS - \mu N = -kT \ln \mathcal{Z} \tag{10.83}$$

where the grand canonical partition function is, in general, given by

$$\mathcal{Z}(T, V, \mu) = \operatorname{Tr}\left(\exp\left\{-\beta\left(\hat{H}-\mu\hat{N}\right)\right\}\right) \tag{10.84}$$

and Φ represents the *grand canonical potential.* As in the classical case, the grand canonical density operator can be generalized. If, for instance, the conserved quantity $\hat{O}$ with $\left[\hat{O}, \hat{H}\right] = 0$ no longer possesses a sharp eigenvalue, but is conserved only on average, we have to set

$$\hat{\rho} = \frac{\exp\left\{-\beta\left(\hat{H}-\mu\hat{N}+\alpha\hat{O}\right)\right\}}{\operatorname{Tr}\left(\exp\left\{-\beta\left(\hat{H}-\mu\hat{N}+\alpha\hat{O}\right)\right\}\right)} \tag{10.85}$$

The intensive variable α (Lagrange parameter) is now connected with the average of the operator $\hat{O}$,

$$\left\langle\hat{O}\right\rangle = \operatorname{Tr}\left(\hat{\rho}\hat{O}\right) \tag{10.86}$$

If one fixes the intensive variable $\beta\alpha$, a certain average value of the observable $\hat{O}$ is assumed according to Equation (10.86). This is completely analogous to the fact that a certain mean energy is assumed when the temperature is fixed, or that a mean particle number is assumed when $\mu\beta$ is fixed. On the other hand, for a given average $\left\langle\hat{O}\right\rangle$ one can determine the intensive quantity $\beta\alpha$ from Equation (10.86).

As we see, we just obtain the expressions for the density operators in the energy representation which we had already used earlier for the description of quantum systems in the framework of classical statistics.

Obviously, the introduction of density operators does not yet solve the problem of particles being indistinguishable, for we had obtained in the quantum mechanical, microcanonical calculation of the properties of the ideal gas in Chapter 5 essentially the same result as in the classical case. The result had to be corrected for the Gibbs factor, as did the classical result. We will obtain a solution to this problem and thus a consistent quantum statistical theory only if we regard the fact that identical particles are also indistinguishable in the quantum mechanical states.

Before doing this, we want to calculate the density matrix for some concrete cases.

Example 10.2: Free particle in the momentum representation

We look for the canonical density matrix in the momentum representation for a free particle in a box of volume $V = L^3$ and periodic boundary conditions. The Hamiltonian of a free particle is $\hat{H} = \hat{\vec{p}}^2/2m$, and the energy eigenfunctions are plane waves;

$$\hat{H}\,|\phi_{\vec{k}}\rangle = E\,|\phi_{\vec{k}}\rangle \qquad \text{with} \qquad E = \frac{\hbar^2\vec{k}^2}{2m}$$

and

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}}\exp\left\{i\vec{k}\cdot\vec{r}\right\}, \qquad \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z), \qquad n_i = 0, \pm 1, \pm 2, \ldots. \tag{10.87}$$

The energy eigenvalues are thus discrete, but their mutual separation for macroscopic volumes is so small that one may again return to continuous momenta and energies. The advantage of the formulation using a box and periodic boundary conditions is that we have automatically included in the description a finite volume for the particles, which is not the case for free plane waves.

The functions $\phi_{\vec{k}}(\vec{r})$ are orthonormalized,

$$\langle\phi_{\vec{k}'}|\,\phi_{\vec{k}}\rangle = \delta_{\vec{k}'\vec{k}} = \delta_{n_{x'}n_x}\delta_{n_{y'}n_y}\delta_{n_{z'}n_z}$$

and complete with respect to all periodic functions, the wavelengths of which fulfill Equation (10.87):

$$\sum_{\vec{k}}\phi^*_{\vec{k}}(\vec{r}')\phi_{\vec{k}}(\vec{r}) = \delta(\vec{r}-\vec{r}'), \qquad -\frac{L}{2} \le r_i, \quad r_i' \le \frac{L}{2} \tag{10.88}$$

We first calculate the matrix elements

$$\left\langle\phi_{\vec{k}'}\left|\exp\left\{-\beta\hat{H}\right\}\right|\phi_{\vec{k}}\right\rangle = \exp\left\{-\frac{\beta\hbar^2}{2m}\vec{k}^2\right\}\langle\phi_{\vec{k}'}|\,\phi_{\vec{k}}\rangle = \exp\left\{-\frac{\beta\hbar^2}{2m}\vec{k}^2\right\}\delta_{\vec{k}'\vec{k}} \tag{10.89}$$

One immediately anticipates this, if one inserts the Taylor series expansion for $\exp\left\{-\beta\hat{H}\right\}$. Each term $\hat{H}^n$ then yields the eigenvalue $(\hbar\vec{k})^2/2m)^n$, and the whole expression becomes $\exp\left\{-\beta(\hbar\vec{k})^2/2m)\right\}$. The canonical partition function becomes

$$Z(T, V, 1) = \mathrm{Tr}\exp\left\{-\beta\hat{H}\right\} = \sum_{\vec{k}}\left\langle\phi_{\vec{k}}\left|\exp\left\{-\beta\hat{H}\right\}\right|\phi_{\vec{k}}\right\rangle = \sum_{\vec{k}}\exp\left\{-\frac{\beta\hbar^2}{2m}\vec{k}^2\right\} \tag{10.90}$$

Since, as already mentioned, the eigenvalues $\vec{k}$ lie very close together in a large volume, the calculation of Equation (10.90) can be performed without large error by replacing the sum by an integral.

$$Z(T, V, 1) = \frac{V}{(2\pi)^3}\int d^3\vec{k}\exp\left\{-\frac{\beta\hbar^2}{2m}\vec{k}^2\right\} = \frac{V}{(2\pi)^3}\left(\frac{2m\pi}{\beta\hbar^2}\right)^{3/2} = \frac{V}{\lambda^3} \tag{10.91}$$

The factor $V/(2\pi)^3$ must appear, because Equation (10.88) still has to be fulfilled after replacing the sum by an integral. The partition function is thus identical with the classical result. However, in contrast to the classical calculation of $Z(T, V, 1)$, the factor h^{-3} appears here automatically. Remember: The unit of volume h^{3N} in the phase space for N particles was

obtained in Chapter 5, only for a quantum mechanical system, and then applied for all classical systems.

The matrix elements of the density operator thus become

$$\langle \phi_{\vec{k}'} | \hat{\rho} | \phi_{\vec{k}} \rangle = \frac{\lambda^3}{V} \exp\left\{ -\frac{\beta\hbar^2}{2m} \vec{k}^2 \right\} \delta_{\vec{k}'\vec{k}}$$

Thus, the density matrix is diagonal, and the matrix elements have the same form as the classical momentum distribution.

Example 10.3: Free particle in the coordinate representation

We look for the canonical density matrix in the coordinate representation for a free particle in a box of volume $V = L^3$ and periodic boundary conditions.

In the preceding example, we calculated the matrix elements of $\hat{\rho}$ in the momentum representation. We need only to transform these into the coordinate representation;

$$\left\langle \vec{k}' \middle| \hat{\rho} \middle| \vec{k} \right\rangle = \frac{\lambda^3}{V} \exp\left\{ -\frac{\beta\hbar^2}{2m} \vec{k}^2 \right\} \delta_{\vec{k}'\vec{k}}$$

where for the sake of brevity, we denote only the quantum numbers in the bra and ket vectors.

$$\begin{aligned}
\langle \vec{r}' | \hat{\rho} | \vec{r} \rangle &= \sum_{\vec{k}'\vec{k}} \left\langle \vec{r}' \middle| \vec{k}' \right\rangle \left\langle \vec{k}' \middle| \hat{\rho} \middle| \vec{k} \right\rangle \left\langle \vec{k} \middle| \vec{r} \right\rangle \\
&= \sum_{\vec{k}'\vec{k}} \phi_{\vec{k}'}(\vec{r}') \left(\frac{\lambda^3}{V} \exp\left\{ -\frac{\beta\hbar^2}{2m} \vec{k}^2 \right\} \delta_{\vec{k}'\vec{k}} \right) \phi^*_{\vec{k}}(\vec{r}) \\
&= \frac{\lambda^3}{V} \frac{1}{(2\pi)^3} \int d^3\vec{k} \exp\left\{ -\frac{\beta\hbar^2}{2m} \vec{k}^2 + i\vec{k} \cdot (\vec{r}' - \vec{r}) \right\} \qquad \textbf{(10.92)}
\end{aligned}$$

Here the sum was again replaced by an integral. The integral can be reduced to a Gaussian integral, if one completes the square in the exponent,

$$\begin{aligned}
&-\frac{\beta\hbar^2}{2m} \vec{k}^2 + i\vec{k} \cdot (\vec{r}' - \vec{r}) \\
&= -\frac{\beta\hbar^2}{2m} \left\{ \vec{k}^2 - \frac{2mi}{\beta\hbar^2} (\vec{r}' - \vec{r}) \cdot \vec{k} + \left(\frac{mi}{\beta\hbar^2} \right)^2 (\vec{r}' - \vec{r})^2 \right\} - \frac{m}{2\beta\hbar^2} (\vec{r}' - \vec{r})^2 \\
&= -\frac{\beta\hbar^2}{2m} \left(\vec{k} - \vec{k}_0 \right)^2 - \frac{m}{2\beta\hbar^2} (\vec{r}' - \vec{r})^2 ,
\end{aligned}$$

with the abbreviation $\vec{k}_0 = \frac{mi}{\beta\hbar^2} (\vec{r}' - \vec{r})$. Equation (10.92) thus becomes

$$\langle \vec{r}' | \hat{\rho} | \vec{r} \rangle = \frac{\lambda^3}{V} \frac{1}{(2\pi)^3} \exp\left\{ -\frac{m}{2\beta\hbar^2} (\vec{r}' - \vec{r})^2 \right\} \int d^3\vec{k} \exp\left\{ -\frac{\beta\hbar^2}{2m} \left(\vec{k} - \vec{k}_0 \right)^2 \right\}$$

Now the vector $\vec{k}_0$ is complex, but as one knows, the Gaussian integral does not depend on the position of the center. We thus obtain

$$\langle \vec{r}' | \hat{\rho} | \vec{r} \rangle = \frac{\lambda^3}{V} \frac{1}{(2\pi)^3} \exp\left\{ -\frac{m}{2\beta\hbar^2} (\vec{r}' - \vec{r})^2 \right\} \left(\frac{2m\pi}{\beta\hbar^2} \right)^{3/2}$$

$$= \frac{1}{V} \exp\left\{-\frac{\pi}{\lambda^2}\left(\vec{r}' - \vec{r}\right)^2\right\} \tag{10.93}$$

where we again used the often occurring thermal wavelength $\lambda = \sqrt{h^2/2\pi mkT}$. Hence, in the coordinate representation the density matrix is no longer a diagonal matrix, but a Gaussian function in $(\vec{r}' - \vec{r})$. The diagonal elements of the density matrix in the coordinate representation can be interpreted quite analogously to the preceding example as the respective density distribution in coordinate space. This again agrees with the classical constant density:

$$\langle \vec{r} \,|\hat{\rho}|\, \vec{r} \rangle = \rho(\vec{r}) = \frac{1}{V}$$

The nondiagonal elements $\vec{r} \neq \vec{r}'$ can be interpreted as the transition probability of the particle to move from a position $\vec{r}$ to a new position $\vec{r}'$. These transitions are related to the quantum mechanical uncertainty of nondiagonal observables. They are restricted to spatial regions having the size of the thermal wavelength. For large temperatures ($\lambda \to 0$), this is hardly observable, but for low temperatures, λ may become very large. This is a first hint of the fact that quantum effects play an especially large role at low temperatures.

In the following, we will often need the matrix elements

$$\left\langle \vec{r}' \left| \exp\left\{-\beta \hat{H}\right\} \right| \vec{r} \right\rangle = \frac{1}{\lambda^3} \exp\left\{-\frac{\pi}{\lambda^2}\left(\vec{r}' - \vec{r}\right)^2\right\} = f\left(\vec{r}' - \vec{r}\right) \tag{10.94}$$

wherefore we here introduce the abbreviation $f\left(\vec{r}' - \vec{r}\right)$ for them.

Exercise 10.4: The Wigner transformation

One can assign to each quantum mechanical one-particle operator $\hat{O}(\hat{\vec{r}}, \hat{\vec{p}})$ a corresponding classical observable $O_W(\vec{r}, \vec{p})$ via the so-called *Wigner transformation*, if the matrix elements $\left\langle \vec{r}' \left| \hat{O} \right| \vec{r} \right\rangle$ in the coordinate representation are known:

$$O_W(\vec{R}, \vec{p}) = \int \left\langle \vec{R} - \frac{1}{2}\vec{r} \left| \hat{O} \right| \vec{R} + \frac{1}{2}\vec{r} \right\rangle \exp\left\{\frac{i}{\hbar}\vec{p} \cdot \vec{r}\right\} d^3\vec{r} \tag{10.95}$$

The reverse of the Wigner transformation (10.95) is the *quantization prescription of Weyl*. This allows one to assign to each classical observable $O_W(\vec{r}, \vec{p})$ matrix elements $\left\langle \vec{r}' \left| \hat{O} \right| \vec{r} \right\rangle$ of a quantum mechanical operator $\hat{O}$ in the coordinate representation:

$$\left\langle \vec{r}' \left| \hat{O} \right| \vec{r} \right\rangle = \frac{1}{h^3} \int O_W\left(\frac{1}{2}\left(\vec{r}' + \vec{r}\right), \vec{p}\right) \exp\left\{\frac{i}{\hbar}\vec{p} \cdot \left(\vec{r}\,' - \vec{r}\right)\right\} d^3\vec{p} \tag{10.96}$$

Show that

1) The Wigner tranformation (10.95) of the matrix elements $\langle \vec{r}' \,|\hat{\rho}|\, \vec{r} \rangle$ of the quantum mechanical density operator (10.93) yields the classical canonical phase-space density $\rho(\vec{r}, \vec{p})$.

2) Weyl's quantization prescription, applied to the classical canonical phase-space density, leads to the matrix elements $\langle \vec{r}' \,|\hat{\rho}|\, \vec{r} \rangle$ of the quantum mechanical density operator.

Solution 1) We have to calculate

$$\rho(\vec{R}, \vec{p}\,) = \int \left\langle \vec{R} - \frac{1}{2}\vec{r} \left| \hat{\rho} \right| \vec{R} + \frac{1}{2}\vec{r} \right\rangle \exp\left\{\frac{i}{\hbar}\vec{p} \cdot \vec{r}\right\} d^3\vec{r}$$

with the matrix elements (10.93)

$$\left\langle \vec{R} - \frac{1}{2}\vec{r} \middle| \hat{\rho} \middle| \vec{R} + \frac{1}{2}\vec{r} \right\rangle = \frac{1}{V} \exp\left\{ -\frac{\pi}{\lambda^2}\vec{r}^2 \right\}$$

$$\rho(\vec{R}, \vec{p}) = \frac{1}{V} \int d^3\vec{r} \exp\left\{ -\frac{\pi}{\lambda^2} \left(\vec{r}^2 - 2\frac{i\lambda^2}{h} \vec{p} \cdot \vec{r} \right) \right\} \qquad \textbf{(10.97)}$$

As in the preceding example, we can complete the square in the argument of the exponential function,

$$\vec{r}^2 - 2\frac{i\lambda^2}{h} \vec{p} \cdot \vec{r} = (\vec{r} - \vec{r}_0)^2 - \vec{r}_0^2$$

if we set $\vec{r}_0 = \frac{i\lambda^2}{h} \vec{p}$. Thus Equation (10.97) becomes

$$\rho(\vec{R}, \vec{p}) = \frac{1}{V} \exp\left\{ \frac{\pi}{\lambda^2} \vec{r}_0^2 \right\} \int d^3\vec{r} \exp\left\{ -\frac{\pi}{\lambda^2} (\vec{r} - \vec{r}_0)^2 \right\}$$

The Gaussian integral has the value λ^3. Inserting the expression for $\vec{r}_0$ therefore yields

$$\rho(\vec{R}, \vec{p}) = \frac{\lambda^3}{V} \exp\left\{ -\frac{\pi\lambda^2}{h^2} \vec{p}^2 \right\} = \frac{\lambda^3}{V} \exp\left\{ -\frac{\beta}{2m} \vec{p}^2 \right\} \qquad \textbf{(10.98)}$$

This is just the classical canonical phase-space density (cf. Example 7.4).

2) If one inserts Equation (10.98) into (10.96), one has to calculate

$$\langle \vec{r}' | \hat{\rho} | \vec{r} \rangle = \frac{1}{h^3} \frac{\lambda^3}{V} \int \exp\left\{ -\frac{\beta}{2m} \left(\vec{p}^2 - 2\frac{mi}{\beta\hbar} \vec{p} \cdot (\vec{r}' - \vec{r}) \right) \right\} d^3\vec{p}$$

Again, we can complete the square in the exponent,

$$\vec{p}^2 - 2\frac{mi}{\beta\hbar} \vec{p} \cdot (\vec{r}' - \vec{r}) = (\vec{p} - \vec{p}_0)^2 - \vec{p}_0^2$$

if we set $\vec{p}_0 = \frac{mi}{\beta\hbar} (\vec{r}' - \vec{r})$. It follows that

$$\langle \vec{r}' | \hat{\rho} | \vec{r} \rangle = \frac{1}{h^3} \frac{\lambda^3}{V} \exp\left\{ \frac{\beta}{2m} \vec{p}_0^2 \right\} \int d^3\vec{p} \exp\left\{ -\frac{\beta}{2m} (\vec{p} - \vec{p}_0)^2 \right\}$$

The value of the Gaussian integral is now, with $\lambda = \sqrt{h^2/2\pi mkT}$,

$$\left(\frac{2m\pi}{\beta} \right)^{3/2} = \frac{h^3}{\lambda^3}$$

If in addition, we insert the value of $\vec{p}_0$ in the exponent, we end up with

$$\langle \vec{r}' | \hat{\rho} | \vec{r} \rangle = \frac{1}{V} \exp\left\{ -\frac{m}{2\beta\hbar^2} (\vec{r}' - \vec{r})^2 \right\} = \frac{1}{V} \exp\left\{ -\frac{\pi}{\lambda^2} (\vec{r}' - \vec{r})^2 \right\}$$

which exactly agrees with the matrix elements (10.93).

Exercise 10.5: Calculation of $\langle \hat{H} \rangle$ for a free particle

Calculate the average of the Hamiltonian for the system of a free particle discussed in the preceding examples.

Solution The average is defined as

$$\left\langle \hat{H} \right\rangle = \mathrm{Tr}\left(\hat{\rho}\hat{H}\right)$$

One calculates it most conveniently in the momentum representation,

$$\begin{aligned}
\left\langle \hat{H} \right\rangle &= \sum_{\vec{k},\vec{k}'} \left\langle \vec{k} \left| \hat{\rho} \right| \vec{k}' \right\rangle \left\langle \vec{k}' \left| \hat{H} \right| \vec{k} \right\rangle \\
&= \sum_{\vec{k},\vec{k}'} \left(\frac{\lambda^3}{V} \exp\left\{ -\frac{\beta\hbar^2}{2m}\vec{k}^2 \right\} \delta_{\vec{k}\vec{k}'} \right) \left(\frac{\hbar^2\vec{k}^2}{2m} \delta_{\vec{k}\vec{k}'} \right) \\
&= \frac{\hbar^2}{2m} \frac{\lambda^3}{V} \frac{V}{(2\pi)^3} \int d^3\vec{k}\vec{k}^2 \exp\left\{ -\frac{\beta\hbar^2}{2m}\vec{k}^2 \right\} \\
&= \frac{\hbar^2}{2m} \lambda^3 \frac{2}{(2\pi)^2} \int_0^\infty dk k^4 \exp\left\{ -\frac{\beta\hbar^2}{2m}k^2 \right\}
\end{aligned}$$

With the usual substitution, $x = \frac{\beta\hbar^2}{2m}k^2$, this becomes

$$\left\langle \hat{H} \right\rangle = \frac{\hbar^2\lambda^3}{m} \frac{1}{(2\pi)^2} \frac{1}{2} \left(\frac{2m}{\beta\hbar^2} \right)^{5/2} \int_0^\infty dx x^{3/2} \exp\{-x\}$$

The value of the integral is $\Gamma(5/2) = 3\sqrt{\pi}/4$. If one reorders the factors and uses $\hbar = h/2\pi$, it follows that

$$\left\langle \hat{H} \right\rangle = \frac{3}{2}kT \qquad \textbf{(10.99)}$$

The average of $\hat{H}$ just corresponds to the classical average. This average can, of course, be obtained directly from the partition function

$$Z(T, V, 1) = \frac{V}{\lambda^3}$$

since

$$\left\langle \hat{H} \right\rangle = \frac{\mathrm{Tr}\left(\exp\left\{-\beta\hat{H}\right\}\hat{H}\right)}{\mathrm{Tr}\left(\exp\left\{-\beta\hat{H}\right\}\right)} = -\frac{\partial}{\partial\beta} \ln\left\{\mathrm{Tr}\left(\exp\left\{-\beta\hat{H}\right\}\right)\right\}$$

or

$$\left\langle \hat{H} \right\rangle = U = -\frac{\partial}{\partial\beta} \ln Z(T, V, 1)$$

which, however, leads to the same result (10.99).

Exercise 10.6: Canonical density matrix for N free particles

Calculate the canonical density matrix in the momentum and coordinate representations for N free particles in a box of volume $V = L^3$ with periodic boundary conditions. Assume the many-particle wavefunction to be the product of the one-particle states (10.87).

Solution The many-particle wavefunction

$$\Psi_{\vec{k}_1,\ldots,\vec{k}_N}(\vec{r}_1,\ldots,\vec{r}_N) = \prod_{i=1}^{N} \phi_{\vec{k}_i}(\vec{r}_i) \tag{10.100}$$

is an eigenfunction of the Hamiltonian $\hat{H} = \sum_{i=1}^{N} \hat{\vec{p}}_i^{\,2}/2m$. In the following, we abbreviate the state vector by $\left|\vec{k}_1,\ldots,\vec{k}_N\right\rangle$,

$$\hat{H}\left|\vec{k}_1,\ldots,\vec{k}_N\right\rangle = E\left|\vec{k}_1,\ldots,\vec{k}_N\right\rangle \qquad \text{with} \qquad E = \sum_{i=1}^{N} \frac{\hbar^2\vec{k}_i^{\,2}}{2m}$$

Our aim is now to calculate $\left\langle \vec{k}_1\,',\ldots,\vec{k}_N\,'\left|\hat{\rho}\right|\vec{k}_1,\ldots,\vec{k}_N\right\rangle$. At first, it is quite analogous to Equation (10.89):

$$\left\langle \vec{k}_1\,',\ldots,\vec{k}_N\,'\left|\exp\left\{-\beta\hat{H}\right\}\right|\vec{k}_1,\ldots,\vec{k}_N\right\rangle = \exp\{-\beta E\}\delta_{k_1'k_1}\cdots\delta_{k_N'k_N} \tag{10.101}$$

since the operator $\exp\{-\beta\hat{H}\}$ can be written as a product of one-particle operators, so that also the total matrix element (10.101) becomes a product of matrix elements for each particle. Now the partition function

$$Z(T,V,N) = \mathrm{Tr}\left(\exp\left\{-\beta\hat{H}\right\}\right) = \sum_{\vec{k}_1,\ldots,\vec{k}_N}\left\langle\vec{k}_1,\ldots,\vec{k}_N\left|\exp\left\{-\beta\hat{H}\right\}\right|\vec{k}_1,\ldots,\vec{k}_N\right\rangle$$

has to be calculated. The trace runs over all mutually different energy eigenstates. These are all assumed, if each momentum vector $\vec{k}_i$ assumes all possible values. This partition function also factors,

$$\begin{aligned} Z(T,V,N) &= \prod_{i=1}^{N}\sum_{\vec{k}_i}\left\langle\vec{k}_i\left|\exp\left\{-\frac{\beta}{2m}\vec{p}_i^{\,2}\right\}\right|\vec{k}_i\right\rangle \\ &= \prod_{i=1}^{N} Z(T,V,1) = [Z(T,V,1)]^N \end{aligned}$$

We thus get with Equation 10.91 of Example 10.2

$$Z(T,V,N) = \frac{V^N}{\lambda^{3N}} \tag{10.102}$$

If one compares Equation (10.102) with the classical result (7.50) one notices that the Gibbs correction factor is missing. The introduction of the density matrix is thus, as already guessed, in fact not sufficient to remove the problem that identical quantum mechanical particles are indistinguishable. The reason is that in the wavefunction (10.100), the particles are still considered distinguishable. The wavefunction (10.100) just represents the fact that particle no. 1 has momentum $\hbar\vec{k}_1$, particle no. 2 has momentum $\hbar\vec{k}_2$, etc. In reality, however, one is not able to tell which particle of a quantum system occupies which one-particle state. Thus, the mistake is caused by the too naive *Ansatz* for the many-particle wavefunction. This is an eigenfunction of the Hamiltonian, but each other wavefunction, which follows from the first by renumbering coordinates (or momenta), is also such an eigenfunction. In the next section we will extensively discuss this problem.

With Equations (10.101) and (10.102), the density matrix reads

$$\left\langle \vec{k}_1\,', \ldots, \vec{k}_N\,' \left| \hat{\rho} \right| \vec{k}_1, \ldots, \vec{k}_N \right\rangle = \prod_{i=1}^{N} \left(\frac{\lambda^3}{V} \exp\left\{ -\frac{\beta\hbar^2}{2m} \vec{k}_i^{\,2} \right\} \delta_{\vec{k}_i'\vec{k}_i} \right) \tag{10.103}$$

As suggested above, we also want to transform Equation (10.103) into the coordinate representation:

$$\begin{aligned} &\left\langle \vec{r}_1\,', \ldots, \vec{r}_N\,' \left| \hat{\rho} \right| \vec{r}_1, \ldots, \vec{r}_N \right\rangle \\ &\quad = \sum_{\vec{k}_1\,', \ldots, \vec{k}_N\,'} \sum_{\vec{k}_1, \ldots, \vec{k}_N} \left\langle \vec{r}_1\,', \ldots, \vec{r}_N\,' \middle| \vec{k}_1\,', \ldots, \vec{k}_N\,' \right\rangle \\ &\quad \times \left\langle \vec{k}_1\,', \ldots, \vec{k}_N\,' \left| \hat{\rho} \right| \vec{k}_1, \ldots, \vec{k}_N \right\rangle \left\langle \vec{k}_1, \ldots, \vec{k}_N \middle| \vec{r}_1, \ldots, \vec{r}_N \right\rangle \end{aligned} \tag{10.104}$$

Here the closure relation

$$\sum_{\vec{k}_1, \ldots, \vec{k}_N} \left| \vec{k}_1, \ldots, \vec{k}_N \right\rangle \left\langle \vec{k}_1, \ldots, \vec{k}_N \right| = 1$$

was inserted twice. By insertion of the wavefunction and Equation (10.103), Equation (10.104) becomes

$$\begin{aligned} \left\langle \vec{r}_1\,', \ldots, \vec{r}_N\,' \left| \hat{\rho} \right| \vec{r}_1, \ldots, \vec{r}_N \right\rangle &= \sum_{\vec{k}_1\,', \ldots, \vec{k}_N\,'} \sum_{\vec{k}_1, \ldots, \vec{k}_N} \left(\prod_{i=1}^{N} \phi_{\vec{k}_i'}(\vec{r}_i') \right) \\ &\quad \times \prod_{i=1}^{N} \left(\frac{\lambda^3}{V} \exp\left\{ -\frac{\beta\hbar^2}{2m} \vec{k}_i^{\,2} \right\} \delta_{\vec{k}_i'\vec{k}_i} \right) \left(\prod_{i=1}^{N} \phi_{\vec{k}_i}^*(\vec{r}_i) \right) \\ &= \frac{\lambda^{3N}}{V^N} \sum_{\vec{k}_1, \ldots, \vec{k}_N} \prod_{i=1}^{N} \phi_{\vec{k}_i}(\vec{r}_i') \exp\left\{ -\frac{\beta\hbar^2}{2m} \vec{k}_i^{\,2} \right\} \phi_{\vec{k}_i}^*(\vec{r}_i) \\ &= \frac{\lambda^{3N}}{V^N} \prod_{i=1}^{N} \left(\sum_{\vec{k}_i} \phi_{\vec{k}_i}(\vec{r}_i') \exp\left\{ -\frac{\beta\hbar^2}{2m} \vec{k}_i^{\,2} \right\} \phi_{\vec{k}_i}^*(\vec{r}_i) \right) \end{aligned} \tag{10.105}$$

In the bracket expression (10.92) for particle i appears. Therefore, the matrix element (10.105) is also simply the product of the one-particle matrix elements,

$$\left\langle \vec{r}_1\,', \ldots, \vec{r}_N\,' \left| \hat{\rho} \right| \vec{r}_1, \ldots, \vec{r}_N \right\rangle = \prod_{i=1}^{N} \left(\frac{1}{V} \exp\left\{ -\frac{\pi}{\lambda^2} (\vec{r}_i' - \vec{r}_i)^2 \right\} \right) \tag{10.106}$$

Exercise 10.7: Density matrix of a harmonic oscillator

Calculate the density matrix of a harmonic oscillator in the energy and coordinate representations. Study the limiting cases $T \to \infty$ and $T \to 0$.

Hint: The energy eigenfunctions in the coordinate representation are

$$\Psi_n(q) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \frac{H_n(x)}{\sqrt{2^n n!}} \exp\left\{ -\frac{1}{2} x^2 \right\} \tag{10.107}$$

with $x = \sqrt{m\omega/\hbar}q$ and the energy eigenvalues $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$. Use the integral representation

$$H_n(x) = (-)^n \exp\{x^2\}\left(\frac{d}{dx}\right)^n \exp\{-x^2\}$$

$$= \frac{\exp\{x^2\}}{\sqrt{\pi}} \int_{-\infty}^{+\infty} (-2iu)^n \exp\{-u^2 + 2ixu\}\, du \qquad \textbf{(10.108)}$$

Solution The density matrix in the energy representation is trivial:

$$\rho_{mn} = \rho_n \delta_{mn} \qquad \text{with} \qquad \rho_n = \frac{1}{Z} \exp\left\{-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right\}, \qquad n = 0, 1, 2, \ldots$$

where

$$Z(T, V, 1) = \mathrm{Tr}\left(\exp\left\{-\beta\hat{H}\right\}\right) = \sum_n \exp\left\{-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right\}$$

$$= \left[2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right]^{-1}$$

was already calculated in Example 8.1.

On the other hand, the coordinate representation is somewhat more difficult to obtain:

$$\langle q' | \hat{\rho} | q \rangle = \sum_{nn'} \langle q' | n' \rangle \langle n' | \hat{\rho} | n \rangle \langle n | q \rangle$$

Here we have twice inserted the complete set of energy eigenfunctions (10.107).

$$\langle q' | \hat{\rho} | q \rangle = \sum_{nn'} \Psi_{n'}(q')\rho_{nn'}\Psi_n^*(q)$$

$$= \frac{1}{Z} \sum_n \exp\left\{-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right\} \Psi_n^*(q)\Psi_n(q')$$

$$= \frac{1}{Z}\left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \exp\left\{-\frac{1}{2}\left(x^2 + x'^2\right)\right\}$$

$$\sum_{n=0}^{\infty} \frac{1}{2^n n!} \exp\left\{-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right\} H_n(x)H_n(x')$$

Here one now inserts the integral representation (10.108) of the H_n,

$$\langle q' | \hat{\rho} | q \rangle = \frac{1}{Z\pi}\left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \exp\left\{+\frac{1}{2}\left(x^2 + x'^2\right)\right\} \int_{-\infty}^{+\infty} du \int_{-\infty}^{+\infty} dv \sum_{n=0}^{\infty} \frac{(-2uv)^n}{n!}$$

$$\exp\left\{-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right\} \exp\{-u^2 + 2ixu\} \exp\{-v^2 + 2ix'v\} \qquad \textbf{(10.109)}$$

The summation over n can be carried out, since

$$\sum_{n=0}^{\infty} \frac{(-2uv)^n}{n!} \exp\left\{-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right\}$$

$$= \exp\left\{-\frac{1}{2}\beta\hbar\omega\right\} \sum_{n=0}^{\infty} \frac{1}{n!} \left(-2uv \exp\{-\beta\hbar\omega\}\right)^n$$

$$= \exp\left\{-\frac{1}{2}\beta\hbar\omega\right\} \exp\left\{-2uv \exp\{-\beta\hbar\omega\}\right\}$$

Thus Equation (10.109) becomes

$$\langle q' | \hat{\rho} | q \rangle = \frac{1}{Z\pi} \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \exp\left\{+\frac{1}{2}\left(x^2 + x'^2 - \beta\hbar\omega\right)\right\} \int_{-\infty}^{+\infty} du \int_{-\infty}^{+\infty} dv$$
$$\exp\left\{-u^2 + 2ixu - v^2 + 2ix'v - 2uv \exp\{-\beta\hbar\omega\}\right\}$$

The argument of the exponent is a general quadratic form, which can be also written in the form

$$-u^2 + 2ixu - v^2 + 2ix'v - 2uv \exp\{-\beta\hbar\omega\} = -\frac{1}{2}\vec{w}^T \hat{A} \vec{w} + i\vec{b} \cdot \vec{w}$$

if we put

$$\hat{A} = 2\begin{pmatrix} 1 & \exp\{-\beta\hbar\omega\} \\ \exp\{-\beta\hbar\omega\} & 1 \end{pmatrix}, \qquad \vec{b} = 2\begin{pmatrix} x \\ x' \end{pmatrix}, \qquad \vec{w} = \begin{pmatrix} u \\ v \end{pmatrix}$$

Now the general formula

$$\int d^n\vec{w} \exp\left\{-\frac{1}{2}\vec{w}^T \hat{A} \vec{w} + i\vec{b} \cdot \vec{w}\right\} = \frac{(2\pi)^{n/2}}{\left[\det \hat{A}\right]^{1/2}} \exp\left\{-\frac{1}{2}\vec{b}^T \hat{A}^{-1} \vec{b}\right\} \qquad \textbf{(10.110)}$$

holds, if $\hat{A}$ is an invertible symmetric matrix.

One proves this as follows: At first one substitutes the new variable $\vec{z} = \vec{w} - i\vec{y}$, where the vector $\vec{y}$ is defined by $\vec{y} = \hat{A}^{-1}\vec{b}$. The Jacobian determinant of this transformation has the absolute value 1, so that no additional factors appear in the integrand. Then it holds that

$$-\frac{1}{2}\vec{w}^T \hat{A} \vec{w} + i\vec{b} \cdot \vec{w} = -\frac{1}{2}(\vec{z} + i\vec{y})^T \hat{A} (\vec{z} + i\vec{y}) + i\vec{b} \cdot (\vec{z} + i\vec{y})$$

$$= -\frac{1}{2}\vec{z}^T \hat{A} \vec{z} - \frac{i}{2}\left(\vec{y}^T \hat{A} \vec{z} + \vec{z}^T \hat{A} \vec{y}\right) + \frac{1}{2}\vec{y}^T \hat{A} \vec{y} + i\vec{b} \cdot \vec{z} - \vec{b} \cdot \vec{y}$$

$$= -\frac{1}{2}\vec{z}^T \hat{A} \vec{z} - \frac{1}{2}\vec{b}^T \hat{A}^{-1} \vec{b}$$

In the second line, the second and the next-to-last terms cancel each other because $\vec{b} \cdot \vec{z} = \vec{b}^T \vec{z}$. The third and last terms can be recombined as well because $\vec{b} \cdot \vec{y} = \vec{b}^T \vec{y}$. The second term in the third line no longer depends on $\vec{z}$, and can be brought in front of the integral, while the first term is a pure quadratic form. For each symmetric matrix $\hat{A}$, there exists an orthogonal matrix $\hat{O}$ with $\hat{O}^{-1} = \hat{O}^T$ and $\det \hat{O} = 1$, so that

$$\hat{O}^T \hat{A} \hat{O} = \mathrm{diag}(\lambda_1, \ldots, \lambda_n)$$

is a diagonal matrix with the eigenvalues on the diagonal. With the new variable $\vec{s} = \hat{O}^{-1}\vec{z}$ one obtains

$$\int d^n\vec{z} \exp\left\{-\frac{1}{2}\vec{z}^T\hat{A}\vec{z}\right\} = \int d^n\vec{s} \exp\left\{-\frac{1}{2}\sum_{i=1}^{n}\lambda_i s_i^2\right\} = \prod_{i=1}^{n}\sqrt{\frac{2\pi}{\lambda_i}}$$

The Jacobian determinant of the transformation $\vec{z} \to \vec{s}$ is just the determinant of $\hat{O}$, which has, however, the absolute value 1, so that again no additional factors appear. The product of the eigenvalues, however, is equal to the determinant of $\hat{A}$, since $\det \hat{A} = \det\left\{\hat{A}\hat{O}\hat{O}^{-1}\right\} = \det\left\{\hat{O}^{-1}\hat{A}\hat{O}\right\} = \det\left\{\hat{O}^T\hat{A}\hat{O}\right\} = \det\{\mathrm{diag}(\lambda_1, \ldots, \lambda_n)\}$, hence Equation (10.110) is proven. With

$$\hat{A}^{-1} = \frac{1}{2(1 - \exp\{-2\beta\hbar\omega\})}\begin{pmatrix} 1 & -\exp\{-\beta\hbar\omega\} \\ -\exp\{-\beta\hbar\omega\} & 1 \end{pmatrix}$$

$$\det \hat{A} = 4(1 - \exp\{-2\beta\hbar\omega\})$$

one obtains $-\frac{1}{2}\vec{b}^T\hat{A}^{-1}\vec{b} = -(1 - \exp\{-2\beta\hbar\omega\})^{-1}\left(x^2 + x'^2 - 2xx'\exp\{-\beta\hbar\omega\}\right)$,

$$\langle q'|\hat{\rho}|q\rangle = \frac{1}{Z}\left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\frac{\exp\left\{-\frac{1}{2}\beta\hbar\omega\right\}}{(1 - \exp\{-2\beta\hbar\omega\})^{1/2}}$$

$$\times \exp\left\{\frac{1}{2}\left(x^2 + x'^2\right) - (1 - \exp\{-2\beta\hbar\omega\})^{-1}\right.$$

$$\left.\left(x^2 + x'^2 - 2xx'\exp\{-\beta\hbar\omega\}\right)\right\}$$

$$\langle q'|\hat{\rho}|q\rangle = \frac{1}{Z}\left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{1/2}\exp\left\{-\frac{1}{2}\left(x^2 + x'^2\right)\coth(\beta\hbar\omega) + \frac{xx'}{\sinh(\beta\hbar\omega)}\right\}$$

If one here exploits the identity

$$\tanh\left(\frac{1}{2}\beta\hbar\omega\right) = \{\cosh(\beta\hbar\omega) - 1\}(\sinh(\beta\hbar\omega))^{-1} = \frac{\sinh(\beta\hbar\omega)}{1 + \cosh(\beta\hbar\omega)}$$

one finally gets

$$\langle q'|\hat{\rho}|q\rangle = \frac{1}{Z}\left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{1/2}$$

$$\times \exp\left\{-\frac{m\omega}{4\hbar}\left[(q + q')^2\tanh\left(\frac{1}{2}\beta\hbar\omega\right)\right.\right.$$

$$\left.\left. + \ (q - q')^2\coth\left(\frac{1}{2}\beta\hbar\omega\right)\right]\right\} \qquad \textbf{(10.111)}$$

The diagonal elements of the density matrix in the coordinate representation yield directly the average density distribution of a quantum mechanical oscillator of temperature T:

$$\rho(q) = \left[\frac{m\omega}{\pi\hbar}\tanh\left(\frac{1}{2}\beta\hbar\omega\right)\right]^{1/2}\exp\left\{-\frac{m\omega}{\hbar}\tanh\left(\frac{1}{2}\beta\hbar\omega\right)q^2\right\}$$

This is a Gaussian distribution with width

$$\sigma_q = \left[\frac{\hbar}{2m\omega \tanh\left(\frac{1}{2}\beta\hbar\omega\right)} \right]^{1/2}$$

In the limit of high temperatures, $\beta\hbar\omega \ll 1$, one has $\tanh\left(\frac{1}{2}\beta\hbar\omega\right) \approx \frac{1}{2}\beta\hbar\omega$ and therefore

$$\rho(q) \approx \left(\frac{m\omega^2}{2\pi kT}\right)^{1/2} \exp\left\{-\frac{m\omega^2 q^2}{2kT}\right\}$$

This is just the classical distribution, which one can obtain also from the classical phase-space density.

In the other limiting case, $\beta\hbar\omega \gg 1$, one has $\tanh\left(\frac{1}{2}\beta\hbar\omega\right) \approx 1$ and

$$\rho(q) \approx \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \exp\left\{-\frac{m\omega q^2}{\hbar}\right\}$$

This is the purely quantum mechanical density distribution of an oscillator in the ground state ($T \to 0$).

The density matrix (10.111) thus contains, for high temperatures, the classical limit, and for very low temperatures, the quantum mechanical ground state density.

11 The Symmetry Character of Many-Particle Wavefunctions

We now want to turn to our often-announced solution of the problem of the principle of indistinguishability of identical particles. This property of quantum mechanical objects cannot be readily understood from a classical point of view. In classical mechanics it is always possible (at least theoretically) to determine at each time all coordinates and momenta of the particles. Therefore, one can follow the path of each particle in phase space during the course of time. The particles possess an individuality which expresses itself in the fact that they can be enumerated, and in the fact that one exactly knows at each instant the state of motion (coordinates and momentum) which any particle assumes.

In quantum theory however, this enumeration of particles makes no sense, since a particle cannot be located more accurately in phase space than the size h^3 of a phase-space cell. This is, of course, a consequence of the uncertainty relation $\Delta x\, \Delta p \geq h$. Since the particles do not move on individual paths in phase space, but rather are smeared over a whole range with a certain probability, one can determine only the total probability of finding a particle in a phase-space cell. However, one can never decide the question of which particular particle is in the cell.

When discussing the canonical phase-space density, we saw that the indistinguishability of identical particles can at least be implemented in the classical theory subsequently "by hand," which lead us to the Gibbs' correction factor. We also saw that the indistinguishability of particles is closely related to the invariance of the Hamiltonian with respect to a change in enumeration of the particle coordinates and momenta. This invariance of the Hamiltonian has more far-reaching consequences in quantum theory than in classical mechanics. From the lectures on symmetries in quantum mechanics (Volume 2 of this series), it is known that to each symmetry property of the Hamiltonian $\hat{H}$ belongs a further operator which commutes with $\hat{H}$ and can thus be diagonalized simultaneously with $\hat{H}$. This means that the energy eigenfunctions can be constructed in such a way that they are also eigenfunctions of the symmetry operators. It is not difficult to find symmetry operators which belong to the invariance of the Hamiltonian with respect to a change in enumeration. They are just the operators $\hat{P}_{ik}$, which exchange the coordinates $\vec{r}_i$ and $\vec{r}_k$ in the wavefunction:

$$\hat{P}_{ik}\Psi(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_k, \ldots, \vec{r}_N) = \Psi(\vec{r}_1, \ldots, \vec{r}_k, \ldots, \vec{r}_i, \ldots, \vec{r}_N) \tag{11.1}$$

If the Hamiltonian is invariant with respect to a change in enumeration of all particles, it holds that

$$\left[\hat{H}, \hat{P}_{ik}\right] = 0 \qquad \text{for all} \qquad i, k = 1, \ldots, N \qquad \text{with} \quad i \neq k \tag{11.2}$$

The eigenfunctions of the $\hat{P}_{ik}$ have to fulfill

$$\begin{aligned} \hat{P}_{ik}\Psi(\ldots, \vec{r}_i, \ldots, \vec{r}_k, \ldots) &= \lambda\Psi(\ldots, \vec{r}_i, \ldots, \vec{r}_k, \ldots) \\ \Psi(\ldots, \vec{r}_k, \ldots, \vec{r}_i, \ldots) &= \lambda\Psi(\ldots, \vec{r}_i, \ldots, \vec{r}_k, \ldots) \end{aligned} \tag{11.3}$$

where λ stands for the possible eigenvalues of the operator $\hat{P}_{ik}$. If one once again applies the operator $\hat{P}_{ik}$ to Equation (11.3), it holds that

$$\hat{P}_{ik}^2\Psi(\ldots, \vec{r}_i, \ldots, \vec{r}_k, \ldots) \equiv \Psi(\ldots, \vec{r}_i, \ldots, \vec{r}_k, \ldots) = \lambda^2\Psi(\ldots, \vec{r}_i, \ldots, \vec{r}_k, \ldots) \tag{11.4}$$

i.e., the real eigenvalues λ have to fulfill $\lambda^2 = 1$. Thus, the operator $\hat{P}_{ik}$ can have only the eigenvalues $\lambda = \pm 1$. Under an exchange of the coordinates $\vec{r}_i$ and $\vec{r}_k$, the eigenfunctions of the $\hat{P}_{ik}$ can therefore either remain the same ($\lambda = +1$, symmetric wavefunctions), or change their sign ($\lambda = -1$, antisymmetric wavefunctions). A generalization of the pair exchange operator is the permutation operator $\hat{P}$, which generates an arbitrary permutation of the indices:

$$\hat{P}\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \Psi\left(\vec{r}_{P_1}, \vec{r}_{P_2}, \ldots, \vec{r}_{P_N}\right) \tag{11.5}$$

where $P_1, \ldots, P_N$ is a permutation of the numbers $1, \ldots, N$ (actually a separate operator belongs to each permuation, but one mostly speaks of *the* permutation operator). If the Hamiltonian commutes with all $\hat{P}_{ik}$, or equivalently, with the permutation operator, the energy eigenfunctions can be constructed in such a way that they are either completely symmetric or completely antisymmetric under an exchange of two arbitrary coordinates (or particle numbers, respectively).

If one starts from an arbitrary energy eigenfunction $\Psi(\vec{r}_1, \ldots, \vec{r}_N)$, without a well-defined symmetry character, one can obtain the completely symmetric and antisymmetric wavefunctions via

$$\Psi^S(\vec{r}_1, \ldots, \vec{r}_N) = A\sum_P \hat{P}\Psi(\vec{r}_1, \ldots, \vec{r}_N) \tag{11.6}$$

$$\Psi^A(\vec{r}_1, \ldots, \vec{r}_N) = B\sum_P (-1)^P \hat{P}\Psi(\vec{r}_1, \ldots, \vec{r}_N) \tag{11.7}$$

Here one sums over all permutations $P_1, \ldots, P_N$ of the indices $1, \ldots, N$. The sign $(-1)^P$ in Equation (11.7) is defined by

$$(-1)^P = \begin{cases} +1 & \text{Even permutation} \\ -1 & \text{Odd permutation} \end{cases} \tag{11.8}$$

This ensures that Ψ^A remains antisymmetric under the exchange of two indices. The notation *even* and *odd* refers to the number of pair exchanges necessary to obtain a certain permutation. The factors A and B can be determined by the normalization.

It is an experimental fact that nature can be described correctly only by wavefunctions having well-defined symmetry. Moreover, as experience teaches us, the eigenvalue λ always has the same value for each particle species. In other words, in nature there exist obviously two kinds of particles: particles that are described by symmetric wavefunctions and that are called—after the Indian physicist Bose—*bosons*, and particles which are described by antisymmetric wavefunctions and are named *fermions*, after the Italian physicist Fermi.

Exactly as in the classical case, noninteracting systems are simple to treat in quantum mechanics, since the corresponding Hamiltonian splits into a sum of one-particle operators:

$$\hat{H}(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) = \sum_{i=1}^{N} \hat{h}(\vec{r}_i, \vec{p}_i) \tag{11.9}$$

If the eigenvalue problem of the operator $\hat{h}(\vec{r}_i, \vec{p}_i)$

$$\hat{h}\phi_k(\vec{r}) = \epsilon_k \phi_k(\vec{r}) \tag{11.10}$$

is solved, one can construct the total wavefunction from the one-particle functions $\phi_k(\vec{r})$. The most simple eigenfunction of the Hamiltonian (11.9) is

$$\Psi^E_{k_1,\ldots,k_N}(\vec{r}_1, \ldots, \vec{r}_N) = \prod_{i=1}^{N} \phi_{k_i}(\vec{r}_i) \tag{11.11}$$

Here we denote the quantum numbers of the occupied states by an index. The wavefunction has the energy eigenvalue

$$E = \sum_{i=1}^{N} \epsilon_{k_i} \tag{11.12}$$

The product wavefunction (11.11) can be written in a clear way in Dirac's notation, using bra and ket state vectors. The state vector of the many-particle wavefunction can be characterized by the quantum numbers of the occupied states. It is the direct product of the one-particle state vectors:

$$|k_1, \ldots, k_N\rangle = |k_1\rangle\, |k_2\rangle \cdots |k_N\rangle \tag{11.13}$$

The corresponding Hilbert space is the direct sum of the one-particle spaces. Equation (11.13) then means that particle no. 1 is in the quantum state k_1, particle no. 2 in the state k_2, etc. The hermitean conjugated state vector reads

$$\langle k_1, \ldots, k_N| = \langle k_N|\, \langle k_{N-1}| \cdots \langle k_1| \tag{11.14}$$

In Equations (11.13) and (11.14) one always has to take care of the order of the quantum numbers, since here we have assumed that the particles are distinguishable, and it is thus of importance which particle occupies a certain state. The state vectors are orthonormalized,

$$\begin{aligned} \langle k'_1 \cdots k'_N | k_1 \cdots k_N \rangle &= \langle k'_N | \langle k'_{N-1} | \cdots \langle k'_1 | k_1 \rangle \cdots |k_N\rangle \\ &= \langle k'_1 | k_1 \rangle \langle k'_2 | k_2 \rangle \cdots \langle k'_N | k_N \rangle \\ &= \delta(k'_1 - k_1)\delta(k'_2 - k_2) \cdots \delta(k'_N - k_N) \end{aligned} \tag{11.15}$$

and complete,

$$1 = \sum_{k_1 \cdots k_N} |k_1 \cdots k_N\rangle \langle k_1 \cdots k_N| \tag{11.16}$$

if such is the case for the one-particle states. An arbitrary wavefunction (even for interacting systems) can therefore be expanded in terms of the $|k_1 \cdots k_N\rangle$. For discrete quantum numbers, the δ-functions in Equation (11.15) are, of course, to be interpreted as Kronecker symbols. The wavefunction (11.11) follows as the coordinate representation of the state vector

$$\begin{aligned}\Psi^E_{k_1 \cdots k_N}(\vec{r}_1, \ldots, \vec{r}_N) &= \langle \vec{r}_1, \ldots, \vec{r}_N | k_1 \cdots k_N \rangle \\ &= \langle \vec{r}_N | \langle \vec{r}_{N-1} | \cdots \langle \vec{r}_1 | k_1 \rangle |k_2\rangle \cdots |k_N\rangle \\ &= \phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2) \cdots \phi_{k_N}(\vec{r}_N)\end{aligned} \tag{11.17}$$

This wavefunction does not have a well-defined symmetry, since the exchange of two coordinates (or equivalently, two quantum numbers) leads to a completely different wavefunction. On the other hand, the Hamiltonian (11.9) commutes with the permutation operator, and thus we can also construct eigenfunctions with a well-defined symmetry character:

$$\Psi^{S,E}_{k_1 \cdots k_N}(\vec{r}_1, \ldots, \vec{r}_N) = \text{Norm} \sum_P \hat{P}\phi_{k_1}(\vec{r}_1) \cdots \phi_{k_N}(\vec{r}_N) \tag{11.18}$$

$$\Psi^{A,E}_{k_1 \cdots k_N}(\vec{r}_1, \ldots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \hat{P}\phi_{k_1}(\vec{r}_1) \cdots \phi_{k_N}(\vec{r}_N) \tag{11.19}$$

Here one sums over all permutations $P_1, \ldots, P_N$ of $1, \ldots, N$ in the arguments of the one-particle wavefunctions $\phi_n(\vec{r}_n)$. However, one immediately notices that it is irrelevant whether one permutes the indices of the coordinates or of the quantum numbers. The antisymmetric wavefunction (11.19), which describes fermions, can be interpreted as a determinant,

$$\Psi^{A,E}_{k_1 \cdots k_N}(\vec{r}_1, \ldots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \phi_{k_1}(\vec{r}_1) & \cdots & \phi_{k_1}(\vec{r}_N) \\ \vdots & & \vdots \\ \phi_{k_N}(\vec{r}_1) & \cdots & \phi_{k_N}(\vec{r}_N) \end{pmatrix} \tag{11.20}$$

This determinant is also called the *Slater determinant.* Here the well-known *Pauli principle* for fermions becomes immediately obvious, which tells us that two equal fermions cannot occupy the same one-particle state. If this were the case, two of the quantum numbers $k_1, \ldots, k_N$ would be equal, and thus two rows of the determinant would be identical. Then, however, the wavefunction would automatically vanish.

In contrast, arbitrarily many bosons may occupy the same one-particle state. This fact makes the normalization of the symmetric wavefunctions (11.18) more complicated. It namely depends on how many of the quantum numbers $k_1, \ldots, k_N$ are equal. If, for instance, the state k_1 is occupied by n_1 bosons, k_2 by n_2 bosons, etc., where, of course,

$N = \sum_i n_i$, the norm from Equation (11.18) becomes

$$\text{norm} = [N! n_1! n_2! \cdots]^{-1/2} \tag{11.21}$$

This becomes clear, if one considers that there exist all in all exactly $N!$ permutations. However, the n_i mutual permutations of the same quantum numbers lead to the same term in the sum in Equation (11.18).

Example 11.1: Normalization of the symmetric two-particle wavefunction

We calculate the normalization of the symmetric two-particle wavefunction

$$\Psi^S(\vec{r}_1, \vec{r}_2) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)$$

$$\begin{aligned}\Psi^{S*}\Psi^S = {} & \phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2)\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2)\phi_1(\vec{r}_2)\phi_2(\vec{r}_1) \\ & + \phi_1^*(\vec{r}_2)\phi_2^*(\vec{r}_1)\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_1^*(\vec{r}_2)\phi_2^*(\vec{r}_1)\phi_1(\vec{r}_2)\phi_2(\vec{r}_1)\end{aligned}$$

If ϕ_1 and ϕ_2 are orthonormal, the second and third terms vanish when integrating over coordinates, $\langle \Psi^S | \Psi^S \rangle = 2$. If, however, both particles occupy the same state ϕ_1, the mixed terms also contribute, and we obtain $\langle \Psi^S | \Psi^S \rangle = 4$. Both cases are described by the norm $[N! n_1! n_2! \cdots]^{-1/2}$. In the first case, $N = 2, n_1 = 1, n_2 = 1, \ldots$, and in the second case, $N = 2, n_1 = 2, n_2 = 0, \ldots$.

The (anti)symmetrized wavefunctions also can be written more clearly in Dirac's notation,

$$\begin{aligned}|k_1, \ldots, k_N\rangle^A &= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \hat{P} \, |k_1, \ldots, k_N\rangle \\ &= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \left| k_{P_1} \cdots k_{P_N} \right\rangle \end{aligned} \tag{11.22}$$

$$\begin{aligned}|k_1, \ldots, k_N\rangle^S &= \frac{1}{\sqrt{N!S}} \sum_P \hat{P} \, |k_1, \ldots, k_N\rangle \\ &= \frac{1}{\sqrt{N!S}} \sum_P \left| k_{P_1}, \ldots, k_{P_N} \right\rangle \end{aligned} \tag{11.23}$$

Here the factor $S^{-1/2}$ represents the additional normalization, if several of the $k_1, \ldots, k_N$ are equal. One can easily prove, with the help of Equations (11.22) and (11.23), that the (anti)symmetrized wavefunctions have a well-defined symmetry character:

$$\hat{P} \, |k_1, \ldots, k_N\rangle^A = \left| k_{P_1}, \ldots, k_{P_N} \right\rangle^A = (-1)^P \, |k_1, \ldots, k_N\rangle^A \tag{11.24}$$

$$\hat{P} \, |k_1, \ldots, k_N\rangle^S = \left| k_{P_1}, \ldots, k_{P_N} \right\rangle^S = |k_1, \ldots, k_N\rangle^S \tag{11.25}$$

They are even orthonormalized:

$$
\begin{aligned}
&{}^{A}\left\langle k_1' \cdots k_N' \middle| k_1, \ldots, k_N \right\rangle^{A} \\
&\quad = \frac{1}{N!} \sum_{P} (-1)^{P} \sum_{P'} (-1)^{P'} \left\langle k_{P_1'}', \ldots, k_{P_N'}' \middle| k_{P_1}, \ldots, k_{P_N} \right\rangle \\
&\quad = \sum_{P} (-1)^{P} \left\langle k_1', \ldots, k_N' \middle| k_{P_1}, \ldots, k_{P_N} \right\rangle \\
&\quad = \sum_{P} (-1)^{P} \delta(k_1' - k_{P_1}) \delta(k_2' - k_{P_2}) \cdots \delta(k_N' - k_{P_N})
\end{aligned}
\tag{11.26}
$$

Here, we have exploited the fact that the twofold sum over all permutations is equal to $N!$ times the single sum over all permutations, as one readily convinces oneself e.g., for, $N = 2$. Since the right-hand side does not vanish, even if any permutation of $\{k_1, \ldots, k_n\}$ is equal to $\{k_1', \ldots, k_n'\}$, two states which differ only by the order of the quantum numbers are no longer to be considered different (orthonormal).

For the symmetric state vectors, analogously, it holds that

$$
{}^{S}\left\langle k_1' \cdots k_N' \middle| k_1, \ldots, k_N \right\rangle^{S} = \frac{1}{\sqrt{SS'}} \sum_{P} \delta(k_1' - k_{P_1}) \delta(k_2' - k_{P_2}) \cdots \delta(k_N' - k_{P_N})
\tag{11.27}
$$

One readily observes that the additional factor is again necessary, if several quantum numbers are identical. The wavefunctions again follow as coordinate representations of the state vectors

$$
\begin{aligned}
\Psi^{A}_{k_1, \ldots, k_N}(\vec{r}_1, \ldots, \vec{r}_N) &= \frac{1}{\sqrt{N!}} {}^{A}\langle \vec{r}_1, \ldots, \vec{r}_N | k_1, \ldots, k_N \rangle^{A} \\
&= \frac{1}{\sqrt{N!}} \sum_{P} (-1)^{P} \hat{P} \phi_{k_1}(\vec{r}_1) \cdots \phi_{k_N}(\vec{r}_N)
\end{aligned}
\tag{11.28}
$$

$$
\begin{aligned}
\Psi^{S}_{k_1, \ldots, k_N}(\vec{r}_1, \ldots, \vec{r}_N) &= \frac{1}{\sqrt{N!}} {}^{S}\langle \vec{r}_1, \ldots, \vec{r}_N | k_1, \ldots, k_N \rangle^{S} \\
&= \frac{1}{\sqrt{N! n_1! n_2! \cdots}} \sum_{P} \hat{P} \phi_{k_1}(\vec{r}_1) \cdots \phi_{k_N}(\vec{r}_N)
\end{aligned}
\tag{11.29}
$$

The state vectors (11.22) and (11.23) form a complete system in both partial spaces of (anti)symmetrized states. An arbitrary wavefunction (even for interacting systems) can be expanded in terms of these functions:

$$
1^{A} = \frac{1}{N!} \sum_{k_1, \ldots, k_N} |k_1, \ldots, k_N\rangle^{A\,A} \langle k_1, \ldots, k_N| \tag{11.30}
$$

$$
1^{S} = \frac{1}{N!} \sum_{k_1, \ldots, k_N} |k_1, \ldots, k_N\rangle^{S\,S} \langle k_1, \ldots, k_N| \tag{11.31}
$$

Here, 1^{A} and 1^{S} are the unit operators in both partial spaces.

The additional factors $[N!]^{-1/2}$ in Equations (11.28) and (11.29) provide the normalization according to Equations (11.18) and (11.19). On the other hand, these factors cancel in Equations (11.26) and (11.27), since we have two sums over all permutations. One of the sums can be replaced by a factor $N!$, which cancels the two factors $[N!]^{-1/2}$ from Equations (11.22) and (11.23). An additional factor $[N!]^{-1}$ is required in Equations (11.30) and (11.31). Namely, if the quantum numbers $\{k_1, k_2, \ldots k_N\}$ run over all possible values independently from each other, there are sets $\{k_{P_1}, k_{P_2}, \ldots k_{P_N}\}$ in the sums in Equations (11.30) and (11.31) which differ only by the ordering of the quantum numbers, but which correspond to the same microstate. Thus, each microstate is counted $N!$ times in the sums in Equations (11.30) and (11.31).

We now prove that 1^A indeed acts like a unit operator in the space of antisymmetric states. To this end, we show that

$$
\begin{aligned}
&1^A \, |k_1, \ldots, k_N\rangle^A \\
&\quad = \frac{1}{N!} \sum_{k'_1,\ldots,k'_N} |k'_1, \ldots, k'_N\rangle^A \, {}^A\langle k'_1, \ldots, k'_N | \, k_1, \ldots, k_N\rangle^A \\
&\quad = \frac{1}{N!} \sum_{k'_1,\ldots,k'_N} |k'_1, \ldots, k'_N\rangle^A \sum_P (-1)^P \delta(k'_1 - k_{P_1}) \cdots \delta(k'_N - k_{P_N}) \\
&\quad = \frac{1}{N!} \sum_P (-1)^P \, |k_{P_1} \cdots k_{P_N}\rangle^A = \frac{1}{N!} \sum_P |k_1, \ldots, k_N\rangle^A \\
&\quad = |k_1, \ldots, k_N\rangle^A
\end{aligned}
\tag{11.32}
$$

where the relations (11.26) and (11.24) were used. The proof for bosons is analogous; only, in the second line of Equation (11.32) we have to take care of

$$
\sum_{k'_1,\ldots,k'_N} |k'_1, \ldots, k'_N\rangle^S \, \frac{1}{\sqrt{SS'}} \sum_P \delta(k'_1 - k_{P_1}) \cdots \delta(k'_N - k_{P_N}) = \sum_P |k_{P_1} \cdots k_{P_N}\rangle^S \tag{11.33}
$$

Here the additional normalization factor is again necessary, if several quantum numbers are identical.

The (anti)symmetrization of the states also has consequences for the possible observable quantities of the system. For instance, it is now no longer sensible to calculate quantum mechanical expectation values for observables which in some way mark specific particles. For example, it is no longer possible to specify a probability density for finding particle no. 2 at $\vec{r}_1$. There exists only a probability density of finding any of the N particles at $\vec{r}_1$. This means that also *all observables $\hat{O}$ of a system of indistinguishable particles have to be invariant with respect to a change in enumeration of the particles*:

$$
\left[\hat{O}, \hat{P}\right] = 0 \tag{11.34}
$$

The (anti)symmetrized matrix elements of an arbitrary observable can be calculated from the matrix elements with product states:

$$
\begin{aligned}
&{}^{A}\left\langle k'_1, \ldots, k'_N \left| \hat{O} \right| k_1, \ldots, k_N \right\rangle^{A} \\
&= \frac{1}{N!} \sum_P (-1)^P \sum_{P'} (-1)^{P'} \left\langle k'_{P'_1} \cdots k'_{P'_N} \left| \hat{O} \right| k_{P_1} \cdots k_{P_N} \right\rangle \\
&= \sum_P (-1)^P \left\langle k'_1, \ldots, k'_N \left| \hat{O} \right| k_{P_1} \cdots k_{P_N} \right\rangle
\end{aligned}
\tag{11.35}
$$

and analogously for symmetric matrix elements, with

$$
\begin{aligned}
&\left\langle k'_1, \ldots, k'_N \left| \hat{O} \right| k_1, \ldots, k_N \right\rangle \\
&= \int d^3 r_1 \cdots d^3 r_N \phi^*_{k'_1}(\vec{r}_1) \cdots \phi^*_{k'_N}(\vec{r}_N) \hat{O} \phi_{k_1}(\vec{r}_1) \cdots \phi_{k_N}(\vec{r}_N)
\end{aligned}
\tag{11.36}
$$

The calculation of traces of operators follows the prescription

$$
\operatorname{Tr} \hat{O} = \frac{1}{N!} \sum_{k_1, \ldots, k_N} {}^{S,A}\left\langle k_1, \ldots, k_N \left| \hat{O} \right| k_1, \ldots, k_N \right\rangle^{A,S} \tag{11.37}
$$

since now any two states which differ only by a permutation of the quantum numbers must not be counted as different.

The symmetry character of the wavefunction also has important consequences for the thermodynamic and statistical properties of a system. Thus, one speaks of *Bose-Einstein statistics* for bosons and *Fermi-Dirac statistics* for fermions. If a system consists of several distinguishable particle species, the total wavefunction has, of course, only to be (anti)symmetrized with respect to the exchange of two *identical* particles. Then the total basis vectors are products of (anti)symmetrized state vectors. If all particles are considered to be distinguishable, the product states (11.13) may be used. This is the limiting case of classical *Maxwell-Boltzmann statistics*. In many cases, the product states (11.13) may also be used as an approximation for a system of identical (indistinguishable) particles. Then, however, the indistinguishability has to be implemented later on by hand via the Gibbs' correction factor, as we have done up to now. We will soon realize that this approximation can be used very well for systems having low densities and high temperatures. Then quantum statistics (Bose-Einstein or Fermi-Dirac) becomes classical Maxwell-Boltzmann statistics. This is intuitively immediately clear, since for large average distances the wave packets of the particles cannot have a large overlap and thus become approximately distinguishable. On the other hand, quantum effects play a major role at low temperatures and high densities.

We now want to clarify, which particles are actually fermions and which are bosons. This question is answered by the so-called *spin-statistics theorem* of Belinfante (1939)* and Pauli (1940)† According to this theorem, the symmetry character of the wavefunctions

* F. J. Belinfante, *Physica* **6** (1939) 849, 870.

† W. Pauli and F. J. Belinfante, *Physica* **7** (1940) 177.

is related to the spin of the respective particles. The spin-statistics theorem asserts: all particles having half-integer spin are fermions, and all particles having integer spin are bosons. This theorem was at first empirically found. It can, however, also be derived in the framework of relativistic quantum field theory. There one can show that the assumption of wrong symmetry leads to the violation of causality in the theory.

Today one regards all leptons (Greek, meaning *light particles*, e, μ, τ, ν_e, ν_μ, ν_τ, ...) and all quarks (u, d, s, c, b, t, ...) as elementary fermions. On the other hand, quanta which mediate an interaction are bosons (photons for the electromagnetic interaction, $W^\pm$ and Z^0 for the weak interaction, gluons for the strong interaction). This scheme is extended by quanta of collective excitations, like phonons, plasmons, etc. For nonelementary (i.e., composite) particles, one needs to know only the number of fermions contained in the particle. If this is even, the composite particle behaves as a boson (as long as internal degrees of freedom play no role); if it is odd, the composite particle behaves as a fermion.

Example 11.2: Ideal gas

We now want to investigate the modifications needed for the case of the ideal gas of Exercise 10.6, if one uses wavefunctions having well-defined symmetry instead of the product wavefunction. To this end, we first calculate the matrix elements ${}^{A,S}\langle k_1, \ldots, k_N \mid \exp\{-\beta\hat{H}\} \mid k_1, \ldots, k_N\rangle^{A,S}$ in the momentum representation. For the sake of simplicity, we assume that for the symmetric matrix elements, all quantum numbers $k_1', \ldots, k_N'$ and $k_1, \ldots, k_N$ are also different, so that we do not have to constantly carry along the additional normalization factor. If we introduce the symbol $\delta_P = (\pm 1)^P$, the symmetric and antisymmetric state vectors can be written in a uniform way. The upper sign is valid for bosons, the lower for fermions:

$$\left|\vec{k}_1, \ldots, \vec{k}_N\right\rangle^{A,S} = \frac{1}{\sqrt{N!}} \sum_P \delta_P \left|\vec{k}_{P_1}, \ldots, \vec{k}_{P_N}\right\rangle$$

$${}^{A,S}\left\langle \vec{k}_1\,', \ldots, \vec{k}_N\,' \left| \exp\left\{-\beta\hat{H}\right\} \right| \vec{k}_1, \ldots, \vec{k}_N \right\rangle^{A,S}$$

$$= \sum_P \delta_P \left\langle \vec{k}_1\,', \ldots, \vec{k}_N\,' \left| \exp\left\{-\beta\hat{H}\right\} \right| \vec{k}_{P_1}, \ldots, \vec{k}_{P_N} \right\rangle$$

The last matrix element follows immediately from the result (10.101):

$${}^{A,S}\left\langle \vec{k}_1\,', \ldots, \vec{k}_N\,' \left| \exp\left\{-\beta\hat{H}\right\} \right| \vec{k}_1, \ldots, \vec{k}_N \right\rangle^{A,S}$$

$$= \exp\left\{-\frac{\beta\hbar^2}{2m}\left(\vec{k}_1^{\,2} + \cdots + \vec{k}_N^{\,2}\right)\right\} \sum_P \delta_P \delta\left(\vec{k}_1' - \vec{k}_{P_1}\right) \cdots \delta\left(\vec{k}_N' - \vec{k}_{P_N}\right) \qquad \textbf{(11.38)}$$

The partition function

$$Z^{A,S}(T, V, N) = \operatorname{Tr}\left(\exp\left\{-\beta\hat{H}\right\}\right) \qquad \textbf{(11.39)}$$

$$= \frac{1}{N!} \sum_{k_1,\ldots,k_N}^{A,S} \left\langle \vec{k}_1, \ldots, \vec{k}_N \left| \exp\left\{-\beta\hat{H}\right\} \right| \vec{k}_1, \ldots, \vec{k}_N \right\rangle^{A,S}$$

$$= \frac{1}{N!} \sum_{k_1,\ldots,k_N} \sum_P \delta_P \exp\{-\beta E\}\, \delta\left(\vec{k}_1 - \vec{k}_{P_1}\right) \cdots \delta\left(\vec{k}_N - \vec{k}_{P_N}\right)$$

will be investigated in more detail in the next section. Now, we will calculate the coordinate representation ${}^{A,S}\left\langle \vec{r}_1\,', \ldots, \vec{r}_N\,' \left| \exp\left\{-\beta \hat{H}\right\} \right| \vec{r}_1, \ldots, \vec{r}_N \right\rangle^{A,S}$ of the operator $\exp\left\{-\beta \hat{H}\right\}$:

$$\begin{aligned} &{}^{A,S}\left\langle \vec{r}_1\,', \ldots, \vec{r}_N\,' \left| \exp\left\{-\beta \hat{H}\right\} \right| \vec{r}_1, \ldots, \vec{r}_N \right\rangle^{A,S} \\ &= \sum_P \delta_P \left\langle \vec{r}_1\,', \ldots, \vec{r}_N\,' \left| \exp\left\{-\beta \hat{H}\right\} \right| \vec{r}_{P_1}, \ldots, \vec{r}_{P_N} \right\rangle \end{aligned} \tag{11.40}$$

The last matrix element can be obtained from Equation (10.106). If we use abbreviation (10.94), Equation (11.40) becomes

$$\begin{aligned} &{}^{A,S}\left\langle \vec{r}_1\,', \ldots, \vec{r}_N\,' \left| \exp\left\{-\beta \hat{H}\right\} \right| \vec{r}_1, \ldots, \vec{r}_N \right\rangle^{A,S} \\ &= \sum_P \delta_P f\left(\vec{r}\,'_1 - \vec{r}_{P_1}\right) \cdots f\left(\vec{r}\,'_N - \vec{r}_{P_N}\right) \end{aligned}$$

The partition function can, of course, also be calculated in the coordinate representation,

$$\begin{aligned} Z^{A,S}(T, V, N) &= \mathrm{Tr}\left(\exp\left\{-\beta \hat{H}\right\}\right) \\ &= \frac{1}{N!} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N\, {}^{A,S}\left\langle \vec{r}_1, \ldots, \vec{r}_N \left| \exp\left\{-\beta \hat{H}\right\} \right| \vec{r}_1, \ldots, \vec{r}_N \right\rangle^{A,S} \\ &= \frac{1}{N!} \sum_P \delta_P \int d^3\vec{r}_1 \cdots d^3\vec{r}_N\, f\left(\vec{r}_1 - \vec{r}_{P_1}\right) \cdots f\left(\vec{r}_N - \vec{r}_{P_N}\right) \end{aligned} \tag{11.41}$$

To work out the main changes to the prior results obtained using Maxwell-Boltzmann statistics, we consider, for instance, the special system with $N = 2$ particles. Equation (11.38) then reads

$$\begin{aligned} &{}^{A,S}\left\langle \vec{k}'_1, \vec{k}'_2 \left| \exp\left\{-\beta \hat{H}\right\} \right| \vec{k}_1, \vec{k}_2 \right\rangle^{A,S} \\ &= \exp\left\{-\frac{\beta\hbar^2}{2m}\left(\vec{k}_1^{\,2} + \vec{k}_2^{\,2}\right)\right\} \left(\delta\left(\vec{k}'_1 - \vec{k}_1\right) \delta\left(\vec{k}'_2 - \vec{k}_2\right)\right. \\ &\left. \pm \delta\left(\vec{k}'_1 - \vec{k}_2\right) \delta\left(\vec{k}'_2 - \vec{k}_1\right)\right) \end{aligned}$$

and the partition function is

$$Z^{A,S}(T, V, 2) = \frac{1}{2!} \sum_{\vec{k}_1, \vec{k}_2} \exp\left\{-\frac{\beta\hbar^2}{2m}\left(\vec{k}_1^{\,2} + \vec{k}_2^{\,2}\right)\right\} \left(1 \pm \delta\left(\vec{k}_1 - \vec{k}_2\right)\right)$$

(the $\vec{k}_i$ are actually discrete; therefore, one should set $\delta(\vec{k}'_i - \vec{k}_j) = \delta_{\vec{k}'_i, \vec{k}_j}$).

By replacing the sum by an integral, this becomes

$$\begin{aligned} Z^{A,S}(T, V, 2) = &\frac{1}{2} \frac{V^2}{(2\pi)^6} \int d^3k_1\, d^3k_2 \exp\left\{-\frac{\beta\hbar^2}{2m}\left(\vec{k}_1^{\,2} + \vec{k}_2^{\,2}\right)\right\} \\ &\pm \frac{1}{2} \frac{V}{(2\pi)^3} \int d^3k \exp\left\{-\frac{\beta\hbar^2}{m}\vec{k}^{\,2}\right\} \end{aligned} \tag{11.42}$$

We have already calculated the Gaussian integrals occurring in Equation (11.42) several times; we thus obtain

$$Z^{A,S}(T, V, 2) = \frac{1}{2}\frac{V^2}{(2\pi)^6}\left(\frac{2m\pi}{\beta\hbar^2}\right)^3 \pm \frac{1}{2}\frac{V}{(2\pi)^3}\left(\frac{m\pi}{\beta\hbar^2}\right)^{3/2}$$

If we insert here the thermal wavelength $\lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$, the result is

$$Z^{A,S}(T, V, 2) = \frac{1}{2}\frac{V^2}{\lambda^6}\left(1 \pm \frac{1}{2^{3/2}}\frac{\lambda^3}{V}\right) \tag{11.43}$$

This has to be compared with the previous formula

$$Z(T, V, 2) = \frac{1}{2}\frac{V^2}{\lambda^6}$$

according to Equation (10.102) with the Gibbs' factor 1/2!. We observe that the (anti)symmetrization leads, in fact, to correction terms, compared to the classical case. In general, these correction terms represent an expansion with respect to the parameter λ^3/V. The terms become small for systems having large volumes (low densities) and high temperatures. The leading term in front of the parentheses in Equation (11.43) corresponds exactly to the classical result. Unfortunately, the general evaluation of the partition function according to Equation (11.39) is not simple. In the next section we will see that the grand canonical partition function is by far more readily calculated than the canonical partition function.

We now want to investigate in more detail the reasons for the additional terms in the partition function. To this end, we explicitly write down the coordinate representation of $\exp\left\{-\beta\hat{H}\right\}$ for the system of two particles according to Equation (11.41):

$$\begin{aligned}
&{}^{A,S}\left\langle \vec{r}_1', \vec{r}_2' \left| \exp\left\{-\beta\hat{H}\right\} \right| \vec{r}_1, \vec{r}_2 \right\rangle^{A,S} \\
&= f\left(\vec{r}_1' - \vec{r}_1\right) f\left(\vec{r}_2' - \vec{r}_2\right) \pm f\left(\vec{r}_1' - \vec{r}_2\right) f\left(\vec{r}_2' - \vec{r}_1\right) \\
&= \frac{1}{\lambda^6}\left\{\exp\left[-\frac{\pi}{\lambda^2}\left(\left(\vec{r}_1' - \vec{r}_1\right)^2 + \left(\vec{r}_2' - \vec{r}_2\right)^2\right)\right]\right. \\
&\quad \left. \pm \exp\left[-\frac{\pi}{\lambda^2}\left(\left(\vec{r}_1' - \vec{r}_2\right)^2 + \left(\vec{r}_2' - \vec{r}_1\right)^2\right)\right]\right\}
\end{aligned}$$

We already know that the diagonal elements of the density matrix represent the spatial probability densities for the two particles. They read, in this case,

$${}^{A,S}\left\langle \vec{r}_1, \vec{r}_2 \left| \hat{\rho} \right| \vec{r}_1, \vec{r}_2 \right\rangle^{A,S} = \frac{1}{Z^{A,S}\lambda^6}\left[1 \pm \exp\left\{-\frac{2\pi}{\lambda^2}\left(\vec{r}_1 - \vec{r}_2\right)^2\right\}\right] \tag{11.44}$$

Thus, the particles are now no longer homogeneously distributed over the whole space, as they were in the classical case. Bosons and fermions "feel" whether other particles of the same kind are near. If the distance between both particles $|\vec{r}_1 - \vec{r}_2|$ is large compared to the thermal wavelength, the exponential function becomes very small, and one regains the classical result. The probability density for finding the two particles at $\vec{r}_1$ and $\vec{r}_2$ for small distances is, however, larger for bosons and smaller for fermions, compared to the classical case. One can interpret this in terms of an additional attractive potential (for bosons) or repulsive potential (for fermions). This interpretation, of course, has to be applied with care, since the quantum mechanical objects are completely noninteracting, but via the quantum mechanical (anti)symmetrization a classical interaction is simulated.

We can even explicitly construct a potential which influences two classical particles in the same way that the (anti)symmetrization influences the quantum mechanical particles. To this end, we postulate that the matrix elements (11.44) agree with the spatial part of the canonical phase-space density,

$$\rho(\vec{r}_1, \vec{r}_2) \equiv \langle \vec{r}_1, \vec{r}_2 \,|\hat{\rho}|\, \vec{r}_1, \vec{r}_2 \rangle$$

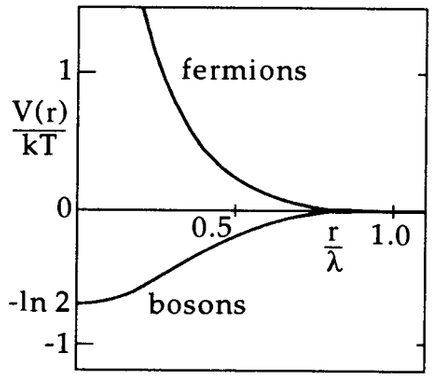


Figure 11.1. Potential to simulate the (anti)symmetrization.

or, if $V(\vec{r}_1, \vec{r}_2)$ denotes the requested pseudo interaction potential, we have, up to normalization factors,

$$\rho(\vec{r}_1, \vec{r}_2) \propto \exp\{-\beta V(\vec{r}_1, \vec{r}_2)\} \equiv 1 \pm \exp\left\{-\frac{2\pi}{\lambda^2}(\vec{r}_1 - \vec{r}_2)^2\right\}$$

The omitted factors yield only an additive constant to the interaction potential:

$$V(\vec{r}_1, \vec{r}_2) = -kT \ln\left[1 \pm \exp\left\{-\frac{2\pi}{\lambda^2}(\vec{r}_1 - \vec{r}_2)^2\right\}\right] \qquad \textbf{(11.45)}$$

The potential (shown in Figure 11.1) is, of course, temperature dependent; thus one already realizes that it is not the usual classical potential. This potential generates the same correlation of particles in coordinate space as the quantum mechanical (anti)symmetrization. Typical quantum mechanical quantities, such as transition probabilities (off-diagonal elements) cannot be described.

For fermions, the potential diverges at $r = 0$, which corresponds to the fact that the probability of finding two fermions at the same place vanishes. We once again emphasize that a classical system of particles with the interaction potential (11.45) is by no means equivalent to quantum statistics.

12 Grand Canonical Description of Ideal Quantum Systems

The formalism of the preceding sections shall now be further worked out for ideal, non-interacting quantum systems. Such systems are described by a Hamiltonian of the form (11.9). The canonical partition function

$$Z(T, V, N) = \mathrm{Tr}\left(\exp\left\{-\beta\hat{H}\right\}\right)$$
$$= \frac{1}{N!}\sum_{k_1,\ldots,k_N}{}^{S,A}\left\langle k_1, \ldots, k_N \left| \exp\left\{-\beta\hat{H}\right\} \right| k_1, \ldots, k_N \right\rangle^{S,A} \qquad (12.1)$$

has to be calculated. The normalization with $N!$ follows according to Equation (11.37). Depending on which type of state vectors is used in Equation (12.1), one obtains the three cases of Maxwell-Boltzmann statistics (MB, product states), Bose-Einstein statistics (BE, symmetric states), and Fermi-Dirac statistics (FD, antisymmetric states). In the first case (MB), the factor $1/N!$ represents the Gibbs' correction factor, while in the two other cases this factor results from the normalization of the state vectors. In principle, the trace (12.1) can be calculated using arbitrary basis states (coordinate representation, momentum representation, etc.), but the energy representation is especially useful. The energy eigenstates fulfill the condition

$$\hat{H}\,|k_1, \ldots, k_N\rangle^{S,A} = E\,|k_1, \ldots, k_N\rangle^{S,A} \qquad \text{with} \qquad E = \sum_{i=1}^{N}\epsilon_{k_i} \qquad (12.2)$$

and the operator $\exp\left\{-\beta\hat{H}\right\}$, applied to these states, yields in all three cases the eigenvalue $\exp\{-\beta E\}$. In the case of Maxwell-Boltzmann statistics, the partition function (12.1) of the N-particle system can be reduced to the evaluation of the one-particle partition function $Z(T, V, 1)$. It holds that

$$Z^{\mathrm{MB}}(T, V, N) = \frac{1}{N!}\prod_{i=1}^{N}\sum_{k_i}\left\langle k_i \left| \exp\left\{-\beta\hat{h}_i\right\} \right| k_i \right\rangle = \frac{1}{N!}\left[Z(T, V, 1)\right]^N \qquad (12.3)$$

if $\hat{h}$ denotes the one-particle Hamiltonian.

We now strive for a similar reduction for the two other cases. To this end, we note that a fully (anti)symmetrized state is already completely characterized if the occupied one-particle states are known. If we enumerate the one-particle state $|k\rangle$ by the index k, it is thus sufficient to know the *occupation numbers* $\{n_1, n_2, \ldots\}$ of each one-particle state in order to determine the N-particle state. For bosons, each occupation number can assume all values $n_k = 0, 1, \ldots, N$. On the other hand, for fermions these numbers are restricted to the values $n_k = 0, 1$ because of Pauli's principle. The occupation numbers must, of course, fulfill the condition

$$\sum_{k=1}^{\infty} n_k = N \tag{12.4}$$

Also, the energy eigenvalue can be expressed in terms of the occupation numbers:

$$E = \sum_{k=1}^{\infty} n_k \epsilon_k \tag{12.5}$$

In contrast to Equation (12.2), the index now runs over all one-particle states, and no longer over all single particles. Quite analogously, the states $|k_1, \ldots, k_N\rangle^{A,S}$ also can be characterized by the occupation numbers, instead of the quantum numbers of the occupied states $k_1, \ldots, k_N$,

$$|n_1, n_2, \ldots\rangle^{S,A} \equiv |k_1, \ldots, k_N\rangle^{S,A} \tag{12.6}$$

Equation (12.6) merely represents a new notation for the basis vectors $|k_1, \ldots, k_N\rangle^{S,A}$. However, the occupation numbers alone do not determine the order in which the quantum numbers $k_1, \ldots, k_N$ appear. Thus, we will now make the agreement that the occupation of the one-particle states is always performed "from below to above." Thus, the quantum numbers $k_1, \ldots, k_N$ shall be arranged in increasing order (different ordering of the quantum numbers, of course, yields only an additional factor $(\pm 1)^P$).

The occupation number representation becomes especially useful in the context of second quantization, which, however, we do not discuss here.

Because of the identity (12.6), the $|n_1, n_2, \ldots\rangle^{S,A}$ fulfill

$$\hat{H}\,|n_1, n_2, \ldots\rangle^{S,A} = E\,|n_1, n_2, \ldots\rangle^{S,A} \qquad \text{with} \qquad E = \sum_{k=1}^{\infty} n_k \epsilon_k \tag{12.7}$$

and

$$\hat{N}\,|n_1, n_2, \ldots\rangle^{S,A} = N\,|n_1, n_2, \ldots\rangle^{S,A} \qquad \text{with} \qquad N = \sum_{k=1}^{\infty} n_k \tag{12.8}$$

where Equation (12.8) can also be interpreted as the definition of a number operator, since this equation determines all the matrix elements of N in the basis $|n_1, n_2, \ldots\rangle^{S,A}$. Since the occupation number n_k of the one-particle state $|k\rangle$ is also an observable quantity, we can define an occupation number operator $\hat{n}_k$ in analogy to Equation (12.8) via

$$\hat{n}_k\,|n_1, n_2, \ldots, n_k, \ldots\rangle^{S,A} = n_k\,|n_1, n_2, \ldots, n_k, \ldots\rangle^{S,A}$$

$$n_k = \begin{cases} 0, 1 & \text{Fermions} \\ 0, 1, 2, \ldots & \text{Bosons} \end{cases} \tag{12.9}$$

The set $\{n_1, n_2, \ldots\}$ and in addition, the specification of the symmetry of the wavefunction uniquely determine the microstate of the system. From this we are then immediately able to construct the respective (anti)symmetrized wavefunction. Two states are therefore identical, if and only if all occupation numbers n_k agree exactly. The orthonormality relation thus reads

$$^{S,A}\langle n_1', n_2', \ldots | n_1, n_2, \ldots \rangle^{S,A} = \delta_{n_1' n_1} \delta_{n_2' n_2} \cdots \tag{12.10}$$

The matrix elements of the density operator have a new, very obvious interpretation in this representation. For the canonical density operator the following is valid:

$$\begin{aligned} &^{S,A}\langle n_1', n_2', \ldots | \hat{\rho} | n_1, n_2, \ldots \rangle^{S,A} \\ &= \frac{1}{Z(T, V, N)} \, ^{S,A}\left\langle n_1', n_2', \ldots \left| \exp\left\{-\beta \hat{H}\right\} \right| n_1, n_2, \ldots \right\rangle^{S,A} \\ &= \frac{1}{Z(T, V, N)} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right\} \delta_{n_1' n_1} \delta_{n_2' n_2} \cdots \end{aligned} \tag{12.11}$$

with

$$Z(T, V, N) = \sum_{\{n_k\}}{}' \exp\left\{-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right\} \tag{12.12}$$

where

$$\sum_{k=1}^{\infty} n_k = N \qquad \text{and} \qquad n_k = \begin{cases} 0, 1 & \text{Fermions} \\ 0, 1, 2, \ldots & \text{Bosons} \end{cases}$$

Here the sum $\sum'$ runs over all allowed sets $\{n_1, n_2, \ldots\}$ of occupation numbers. Each such set corresponds to a microstate of the system. The prime on the summation symbol means that only such occupation numbers contribute which fulfill condition (12.4). Furthermore, for fermions only $n_k = 0, 1$ is allowed, while for bosons one has to sum over the natural numbers. Now we can interpret the diagonal elements of the density matrix,

$$P\{n_k\} = {}^{S,A}\langle n_1, n_2, \ldots | \hat{\rho} | n_1, n_2, \ldots \rangle^{S,A} = \frac{1}{Z} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right\} \tag{12.13}$$

as the probability of finding just the special set $\{n_1, n_2, \ldots\}$ of occupation numbers in the system.

Quite analogously, one obtains for the grand canonical density operator

$$\begin{aligned} &^{S,A}\langle n_1', n_2', \ldots | \hat{\rho} | n_1, n_2, \ldots \rangle^{S,A} \\ &= \frac{1}{\mathcal{Z}(T, V, \mu)} \, ^{S,A}\left\langle n_1', n_2', \ldots \left| \exp\left\{-\beta \left(\hat{H} - \mu \hat{N}\right)\right\} \right| n_1, n_2, \ldots \right\rangle^{S,A} \\ &= \frac{1}{\mathcal{Z}(T, V, \mu)} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k (\epsilon_k - \mu)\right\} \delta_{n_1' n_1} \delta_{n_2' n_2} \cdots \end{aligned} \tag{12.14}$$

with

$$\mathcal{Z}(T, V, \mu) = \sum_{\{n_k\}} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right\} \tag{12.15}$$

$$\text{where } n_k = \begin{cases} 0, 1 & \text{Fermions} \\ 0, 1, 2, \ldots & \text{Bosons} \end{cases}$$

In Equation (12.15) there is no additional constraint on the sum over all occupation numbers, since now one also has to sum over all microstates with different particle numbers N. One readily realizes this, if the grand partition function is written in the form

$$\begin{aligned} \mathcal{Z}(T, V, \mu) &= \sum_{N=0}^{\infty} z^N Z(T, V, N) \\ &= \sum_{N=0}^{\infty} z^N \sum_{\{n_k\}}{}' \exp\left\{-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right\} \\ &= \sum_{N=0}^{\infty} \sum_{\{n_k\}}{}' \exp\left\{-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right\} \end{aligned} \tag{12.16}$$

where the fugacity $z = \exp\{\mu/kT\}$, and $N = \sum_{k=1}^{\infty} n_k$ were used. The primed sum, with the constraint (12.4) and the sum over all particle numbers, however, is equivalent to a sum over all sets of occupation numbers without the constraint. Again, the diagonal matrix elements

$$\begin{aligned} P\{n_k\} &= {}^{S,A}\langle n_1, n_2, \ldots | \hat{\rho} | n_1, n_2, \ldots \rangle^{S,A} \\ &= \frac{1}{\mathcal{Z}} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right\} \end{aligned} \tag{12.17}$$

can be interpreted as the probability of finding the special set $\{n_k\}$ of occupation numbers in a system of the grand canonical ensemble.

It is instructive to apply the language of the occupation number representation also to classical Maxwell-Boltzmann statistics. Here one has to note that the set $\{n_1, n_2, \ldots\}$ does *not* uniquely determine the product wavefunction $|k_1, \ldots, k_N\rangle$, since the occupation numbers do not contain any information about which particle occupies which one-particle state. However, all product states compatible with the set $\{n_1, n_2, \ldots\}$ have the same energy and thus the same probability. We thus have only to count how many such states exist. At first there are $N!$ ways of changing the enumeration of the particles. However, if there are n_k particles in the state $|k\rangle$, then the $n_k!$ permutations of the particles in this one-particle state do not even classically lead to a new macrostate. Each set $\{n_1, n_2, \ldots\}$ thus obtains a weight $N!/(n_1!n_2!\cdots)$, which originates from the distinguishability of the particles. Thus, the canonical partition function of the Maxwell-Boltzmann case can be also calculated in

the occupation number representation:

$$Z^{\mathrm{MB}}(T, V, N) = \frac{1}{N!} \sum_{\{n_k\}}{}' \frac{N!}{n_1! n_2! \cdots} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right\} \tag{12.18}$$

The Gibbs factor $1/N!$ has to be added by hand. Indeed, Equation (12.18) again leads to Equation (12.3), for it can be simplified with the help of the polynomial theorem

$$\begin{aligned} Z^{\mathrm{MB}}(T, V, N) &= \frac{1}{N!} \sum_{n_1, n_2, \ldots = 0}^{N}{}' \frac{N!}{n_1! n_2! \cdots} (\exp\{-\beta\epsilon_1\})^{n_1} (\exp\{-\beta\epsilon_2\})^{n_2} \cdots \\ &= \frac{1}{N!} \left(\sum_{k=1}^{\infty} \exp\{-\beta\epsilon_k\}\right)^N \\ &= \frac{1}{N!} [Z(T, V, 1)]^N \end{aligned} \tag{12.19}$$

If we now define the so-called statistical weight of a set of occupation numbers $\{n_1, n_2, \ldots\}$ by

$$g^{\mathrm{MB}}\{n_k\} = \frac{1}{n_1! n_2! \cdots} \tag{12.20}$$

and corresponding expressions for bosons and fermions,

$$g^{\mathrm{BE}}\{n_k\} = 1 \tag{12.21}$$

as well as

$$g^{\mathrm{FD}}\{n_k\} = \begin{cases} 1 & \text{If all } n_k = 0 \text{ or } 1 \\ 0 & \text{Otherwise} \end{cases} \tag{12.22}$$

then the three cases can be again treated in unique form. The *canonical partition function* is given by

$$Z(T, V, N) = \sum_{\{n_k\}}{}' g\{n_k\} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right\} \tag{12.23}$$

and analogously, the *grand canonical partition function* is given by

$$\mathcal{Z}(T, V, \mu) = \sum_{\{n_k\}} g\{n_k\} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k (\epsilon_k - \mu)\right\} \tag{12.24}$$

The probabilities of Equation (12.13) and (12.17) become

$$P\{n_k\} = \frac{1}{Z} g\{n_k\} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right\} \quad \text{Canonical} \tag{12.25}$$

and

$$P\{n_k\} = \frac{1}{\mathcal{Z}} g\{n_k\} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right\} \quad \text{Grand canonical} \tag{12.26}$$

respectively. Up to now, we have only formulated the problem in another language, but have not arrived at a real simplification. Our aim, however, is to simplify the calculation of the partition function as far as, e.g., the Maxwell-Boltzmann case in Equations (12.19) or (12.3). Unfortunately, such a simplification is not possible for the canonical partition functions in the case of Bose-Einstein or Fermi-Dirac statistics. The additional constraint $N = \sum_{k=1}^{\infty} n_k$ on the sum in Equation (12.23) renders a further simplification more difficult (except in the Maxwell-Boltzmann case). In the grand canonical partition functions, however, this constraint does not appear, and one can thus enormously simplify them also for bosons and fermions. To see this, we write Equation (12.24) for both cases, Bose-Einstein and Fermi-Dirac. For the former, we have

$$\begin{aligned} \mathcal{Z}^{\mathrm{BE}}(T, V, \mu) &= \sum_{n_1, n_2, \ldots = 0}^{\infty} (\exp\{-\beta(\epsilon_1 - \mu)\})^{n_1} (\exp\{-\beta(\epsilon_2 - \mu)\})^{n_2} \cdots \\ &= \prod_{k=1}^{\infty} \sum_{n_k=0}^{\infty} (\exp\{-\beta(\epsilon_k - \mu)\})^{n_k} \end{aligned} \tag{12.27}$$

The sum is a geometric series, and has the value

$$\sum_{n_k=0}^{\infty} (\exp\{-\beta(\epsilon_k - \mu)\})^{n_k} = \left[1 - z \exp\{-\beta\epsilon_k\}\right]^{-1} \tag{12.28}$$

where $z = \exp\{\beta\mu\}$. It follows that

$$\mathcal{Z}^{\mathrm{BE}}(T, V, \mu) = \prod_{k=1}^{\infty} \frac{1}{1 - z \exp\{-\beta\epsilon_k\}} \tag{12.29}$$

For Fermi-Dirac statistics, one obtains, with 1 as upper limit of summation,

$$\begin{aligned} \mathcal{Z}^{\mathrm{FD}}(T, V, \mu) &= \sum_{n_1, n_2, \ldots = 0}^{1} (\exp\{-\beta(\epsilon_1 - \mu)\})^{n_1} (\exp\{-\beta(\epsilon_2 - \mu)\})^{n_2} \cdots \\ &= \prod_{k=1}^{\infty} \sum_{n_k=0}^{1} (\exp\{-\beta(\epsilon_k - \mu)\})^{n_k} \\ &= \prod_{k=1}^{\infty} (1 + z \exp\{-\beta\epsilon_k\}) \end{aligned} \tag{12.30}$$

For the sake of completeness, we again give the grand canonical partition function for Boltzmann particles,

$$\begin{aligned}\mathcal{Z}^{\mathrm{MB}}(T, V, \mu) &= \sum_{n_1,n_2,\ldots=0}^{\infty} \frac{1}{n_1!n_2!\cdots} (\exp\{-\beta(\epsilon_1 - \mu)\})^{n_1} (\exp\{-\beta(\epsilon_2 - \mu)\})^{n_2} \cdots \\ &= \prod_{k=1}^{\infty} \sum_{n_k=0}^{\infty} \frac{1}{n_k!} (\exp\{-\beta(\epsilon_k - \mu)\})^{n_k} \\ &= \prod_{k=1}^{\infty} \exp\{z \exp\{-\beta\epsilon_k\}\} \end{aligned} \tag{12.31}$$

which, of course, agrees with Equation (9.43).

In principle one can calculate also the canonical partition function from the grand canonical partition function with Equation (9.88). However, the integrals appearing in this procedure are rather complicated. On the other hand, this is not even necessary, since the grand canonical ensemble describes the thermodynamic properties of a system as well as the microcanonical or the canonical. In many cases, however, the chemical potential μ or the fugacity z of a system are not given, but the particle number is given. This renders the explicit calculation of the properties of ideal quantum gases at given N more difficult, but is not a principle problem, as we will soon observe.

From the knowledge of the grand canonical partition function one immediately obtains the grand canonical potential

$$\Phi(T, V, \mu) = -kT \ln \mathcal{Z}(T, V, \mu) = U - TS - \mu N = -pV \tag{12.32}$$

with the equations of state (4.113):

$$\begin{aligned} S(T, V, \mu) &= -\left.\frac{\partial \Phi}{\partial T}\right|_{V,\mu} \\ p(T, V, \mu) &= -\left.\frac{\partial \Phi}{\partial V}\right|_{T,\mu} \\ N(T, V, \mu) &= -\left.\frac{\partial \Phi}{\partial \mu}\right|_{T,V} \end{aligned} \tag{12.33}$$

The grand canonical potentials read in detail (with $z = \exp\{\beta\mu\}$)

$$\begin{aligned}\Phi^{\mathrm{MB}}(T, V, \mu) &= -kT \sum_{k=1}^{\infty} z \exp\{-\beta\epsilon_k\} \\ &= -kT \sum_{k=1}^{\infty} \exp\{-\beta(\epsilon_k - \mu)\} \end{aligned} \tag{12.34}$$

$$\Phi^{\mathrm{BE}}(T, V, \mu) = kT \sum_{k=1}^{\infty} \ln(1 - z \exp\{-\beta\epsilon_k\})$$

$$= kT \sum_{k=1}^{\infty} \ln\left(1 - \exp\{-\beta(\epsilon_k - \mu)\}\right) \tag{12.35}$$

$$\Phi^{\mathrm{FD}}(T, V, \mu) = -kT \sum_{k=1}^{\infty} \ln(1 + z \exp\{-\beta\epsilon_k\})$$

$$= -kT \sum_{k=1}^{\infty} \ln\left(1 + \exp\{-\beta(\epsilon_k - \mu)\}\right) \tag{12.36}$$

One can summarize these three cases in one equation:

$$\ln \mathcal{Z} = \frac{pV}{kT} = \frac{1}{a} \sum_{k=1}^{\infty} \ln(1 + az \exp\{-\beta\epsilon_k\}) \tag{12.37}$$

if one defines

$$a = \begin{cases} +1 & FD \\ 0 & MB \\ -1 & BE \end{cases} \tag{12.38}$$

The case $a = 0$ is to be understood as the limit $\lim_{a \to 0}$. The notation (12.37) and (12.38) makes it again possible to investigate the three cases together.

It is very convenient to give expressions of the form (12.37) also for the thermodynamic quantities $N(T, V, \mu) = \left\langle \hat{N} \right\rangle$ and $U(T, V, \mu) = \left\langle \hat{H} \right\rangle$,

$$N(T, V, \mu) = kT \left. \frac{\partial}{\partial \mu} \ln \mathcal{Z} \right|_{T,V} = \sum_{k=1}^{\infty} \frac{1}{z^{-1} \exp\{\beta\epsilon_k\} + a} \tag{12.39}$$

$$U(T, V, \mu) = - \left. \frac{\partial}{\partial \beta} \ln \mathcal{Z} \right|_{z,V} = \sum_{k=1}^{\infty} \frac{\epsilon_k}{z^{-1} \exp\{\beta\epsilon_k\} + a} \tag{12.40}$$

In Equation (12.40) it is important to note that the fugacity $z = \exp\{\beta\mu\}$ is kept constant. The relations (12.39) and (12.40) also can be obtained directly as statistical averages of the operators $\hat{N}$ and $\hat{H}$, as we will show now.

The average of an arbitrary observable $\hat{O}$ in the grand canonical ensemble is defined by

$$\left\langle \hat{O} \right\rangle = \mathrm{Tr}\left(\hat{\rho}\hat{O}\right) = \frac{\mathrm{Tr}\left(\exp\left\{-\beta\left(\hat{H} - \mu\hat{N}\right)\right\}\hat{O}\right)}{\mathrm{Tr}\left(\exp\left\{-\beta\left(\hat{H} - \mu\hat{N}\right)\right\}\right)}$$

$$= \frac{1}{\mathcal{Z}} \sum_{\{n_k\}} g\{n_k\}^{S,A} \left\langle n_1, n_2, \ldots \left| \exp\left\{-\beta\left(\hat{H} - \mu\hat{N}\right)\right\} \hat{O} \right| n_1, n_2, \ldots \right\rangle^{S,A} \tag{12.41}$$

$$= \frac{1}{\mathcal{Z}} \sum_{\{n_k\}} g\{n_k\} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right\}^{S,A} \left\langle n_1, n_2, \ldots \left| \hat{O} \right| n_1, n_2, \ldots \right\rangle^{S,A}$$

If we denote the expectation value of the observable $\hat{O}$ by

$$O(n_1, n_2, \ldots) = {}^{S,A}\left\langle n_1, n_2, \ldots \left| \hat{O} \right| n_1, n_2, \ldots \right\rangle^{S,A} \tag{12.42}$$

it follows that

$$\left\langle \hat{O} \right\rangle = \frac{1}{\mathcal{Z}} \sum_{\{n_k\}} g\{n_k\} \exp\left\{ -\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu) \right\} O(n_1, n_2, \ldots) \tag{12.43}$$

The average of the particle number operator thus becomes

$$\begin{aligned} \left\langle \hat{N} \right\rangle &= \frac{1}{\mathcal{Z}} \sum_{\{n_k\}} g\{n_k\} \exp\left\{ -\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu) \right\} \sum_{k=1}^{\infty} n_k \\ &= \frac{1}{\mathcal{Z}} \left(\frac{1}{\beta} \frac{\partial}{\partial \mu} \sum_{\{n_k\}} g\{n_k\} \exp\left\{ -\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu) \right\} \right)_{T,V} \\ &= \frac{1}{\mathcal{Z}} \, kT \frac{\partial}{\partial \mu} \mathcal{Z} \Big|_{T,V} = kT \frac{\partial}{\partial \mu} \ln \mathcal{Z} \Big|_{T,V} \end{aligned} \tag{12.44}$$

and that of the Hamiltonian becomes

$$\begin{aligned} \left\langle \hat{H} \right\rangle &= \frac{1}{\mathcal{Z}} \sum_{\{n_k\}} g\{n_k\} \exp\left\{ -\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu) \right\} \sum_{k=1}^{\infty} n_k \epsilon_k \\ &= \frac{1}{\mathcal{Z}} \left(-\frac{\partial}{\partial \beta} \sum_{\{n_k\}} g\{n_k\} \exp\left\{ -\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu) \right\} \right)_{z,V} \\ &= -\frac{1}{\mathcal{Z}} \left(\frac{\partial}{\partial \beta} \mathcal{Z} \right)_{z,V} = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} \Big|_{z,V} \end{aligned} \tag{12.45}$$

Here the fugacity $z = \exp\{\mu/kT\}$ is to be considered as constant in the differentiation, as in Equation (9.76). Equations (12.39) and (12.40) can be understood more clearly if we compare them with the general expressions

$$\left\langle \hat{N} \right\rangle = \left\langle \sum_{k=1}^{\infty} \hat{n}_k \right\rangle = \sum_{k=1}^{\infty} \langle \hat{n}_k \rangle \tag{12.46}$$

and

$$\left\langle \hat{H} \right\rangle = \left\langle \sum_{k=1}^{\infty} \hat{n}_k \epsilon_k \right\rangle = \sum_{k=1}^{\infty} \langle \hat{n}_k \rangle \epsilon_k, \tag{12.47}$$

where $\hat{n}_k$ is again the occupation number operator for the one-particle state $|k\rangle$. Obviously, the average of the occupation number is given by

$$\langle \hat{n}_k \rangle = \frac{1}{z^{-1} \exp\{\beta \epsilon_k\} + a} = \frac{1}{\exp\{\beta(\epsilon_k - \mu)\} + a} \tag{12.48}$$

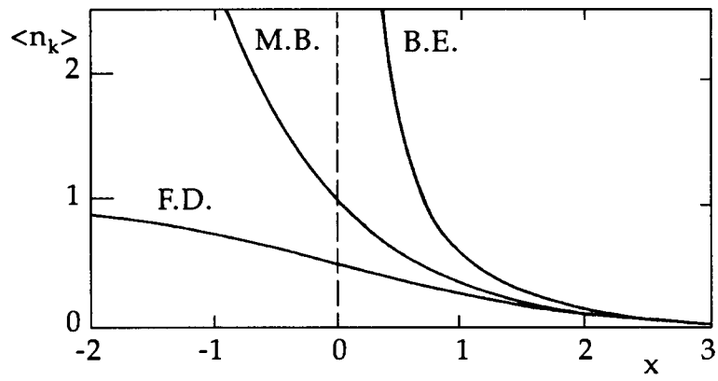


Figure 12.1. Mean occupation number $\langle n_k \rangle$ versus $x = \beta(\epsilon_k - \mu.)$

with a given by Equation (12.38). This can also be directly confirmed, since it holds that

$$\begin{aligned}\langle \hat{n}_k \rangle &= \frac{1}{\mathcal{Z}} \sum_{\{n_k\}} g\{n_k\} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right\} n_k \\ &= \frac{1}{\mathcal{Z}} \left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon_k} \sum_{\{n_k\}} g\{n_k\} \exp\left\{-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right\}\right)_{z,V,\epsilon_{i\neq k}} \\ &= \frac{1}{\mathcal{Z}} \left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon_k} \mathcal{Z}\right)_{z,V,\epsilon_{i\neq k}} = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_k} \ln \mathcal{Z}\Big|_{z,V,\epsilon_{i\neq k}}\end{aligned} \tag{12.49}$$

This prescription for calculating $\langle \hat{n}_k \rangle$ requires further explanation. At first, the fugacity z is to be kept constant when differentiating, exactly as in Equation (12.45). Then, the differentiation with respect to ϵ_k is to be performed in such a way that all other one-particle energies $\epsilon_{i\neq k}$ are also constant. The one-particle energies ϵ_k are determined, of course, by the spectrum of the one-particle Hamiltonian $\hat{h}$. One can now ask how the grand canonical partition function (or ln $\mathcal{Z}$, respectively) changes if one of these levels is slightly shifted; this yields the average occupation number of the level. The application of Equation (12.49) to (12.37) yields Equation (12.48).

We first want to obtain a general overview of the features of the $\langle \hat{n}_k \rangle$. The mean occupation number of the one-particle state $|k\rangle$ is plotted as a function of the dimensionless variable $x = \beta(\epsilon_k - \mu)$ in Figure 12.1. As one observes, for large values of x ($x \gg 1$), all occupation numbers become identical. In this region there is consequently no difference between the classical Maxwell-Boltzmann statistics of distinguishable particles and Bose-Einstein or Fermi-Dirac statistics. One should not be confused that this limit seems to occur for small temperatures ($T \to 0$, $\beta \to \infty$, $\epsilon_k > \mu$). One has to consider that the chemical potential for a given particle number is also a function of temperature, particle number, and volume. For $x \to 0$, the mean occupation number of bosons becomes divergent. Since this case is, of course, unphysical, the chemical potential of a bosonic system always has to be smaller than the energy of the lowest one-particle state. For a given particle number,

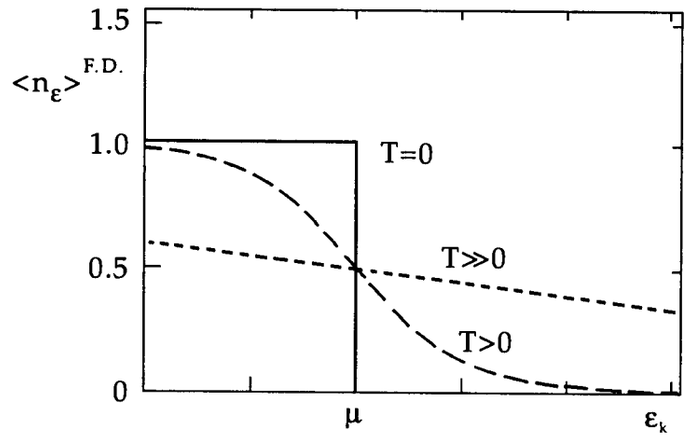


Figure 12.2. Average occupation number of fermions for different temperatures.

the chemical potential has to be determined from Equation (12.39). We will see below that this constraint ($\mu < \epsilon_k$) is always fulfilled.

The average occupation number for fermionic systems is plotted again, for different temperatures, in Figure 12.2. Now, however, the energy ϵ_k of the one-particle state was chosen as the independent variable, at constant chemical potential. The average occupation number $\langle n_k \rangle^{\mathrm{FD}}$ cannot become larger than 1, which is a consequence of the Pauli principle for fermions.

At zero temperature, all states up to the one-particle energy $\epsilon_k = \mu$ are occupied by one particle, and all states with $\epsilon_k > \mu$ are empty. The chemical potential of a fermionic system at $T = 0$ becomes identical with the Fermi energy ϵ_f. This is completely obvious, since at least the energy $\epsilon_f = \mu$ is required to add another fermion to such a system. This fermion has to be placed, of course, in the next empty level, i.e., in a level which is not blocked by the Pauli principle.

For temperatures $T > 0$, more and more fermions are statistically excited into higher levels, and the distribution shown in Figure 12.2 for $T > 0$ is obtained.

Now we calculate the *fluctuations of the occupation numbers*. These are, as usual, measured by the standard deviation $\sigma_{n_k}^2 = \langle \hat{n}_k^2 \rangle - \langle \hat{n}_k \rangle^2$. With the help of Equation (12.49), it is not difficult to calculate the standard deviation,

$$\langle \hat{n}_k^2 \rangle = \frac{1}{\mathcal{Z}} \left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon_k} \right)^2 \mathcal{Z} \Big|_{z,T,\epsilon_{i \neq k}} \tag{12.50}$$

or, because of Equation (12.49),

$$\sigma_{n_k}^2 = \langle \hat{n}_k^2 \rangle - \langle \hat{n}_k \rangle^2 = \left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon_k} \right)^2 \ln \mathcal{Z} \Big|_{z,T,\epsilon_{i \neq k}}$$

$$= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_k} \langle n_k \rangle \Big|_{z,T,\epsilon_{i \neq k}} = \frac{\exp\{\beta(\epsilon_k - \mu)\}}{(\exp\{\beta(\epsilon_k - \mu)\} + a)^2} \tag{12.51}$$

The relative fluctuation with respect to the mean occupation number thus follows as

$$\frac{\sigma_{n_k}^2}{\langle n_k \rangle^2} = \exp\{\beta(\epsilon_k - \mu)\} = z^{-1}\exp\{\beta\epsilon_k\} = \frac{1}{\langle n_k \rangle} - a \tag{12.52}$$

The relative fluctuation (12.52) is thus inversely proportional to the mean occupation number itself. For classical Maxwell-Boltzmann statistics, $a^{\mathrm{MB}} = 0$, one has normal fluctuations. For bosons, $a^{\mathrm{BE}} = -1$, the fluctuations are larger, and for fermions, $a^{\mathrm{FD}} = +1$, the fluctuations are smaller than in the classical case. The reason is that fermions hinder each other when changing one-particle states, while for bosons such fluctuations are advantageous.

We need not be satisfied with the calculation of the relative fluctuations of the occupation numbers alone. One can directly evaluate the probability distribution $p_k(n_k)$ of finding exactly n_k particles in the level k. The mean of this distribution must be given by Equation (12.48).

Example 12.1: The distribution of the occupation number

We consider the energy level ϵ_k as a part of the total system. The other energy levels then represent a particle reservoir. This is just the case of the grand canonical ensemble, now however applied to a system with only one energy level ϵ_k. We want to calculate the probability $p_k(n_k)$ of finding just n_k particles in this subsystem. However, the probability of finding the occupation numbers $\{n_1, n_2, \ldots\}$ in a system of the grand canonical ensemble is given by Equation (12.26). Applied to the subsystem with one level (i.e., with one occupation number n_k) this leads to

$$p\{n_k\} = \frac{g\{n_k\}\exp\{-\beta(E - \mu N)\}}{\sum_{\{n_k\}} g\{n_k\}\exp\{-\beta(E - \mu N)\}} = \frac{g_{n_k}\exp\{-\beta n_k(\epsilon_k - \mu)\}}{\sum_{n_k} g_{n_k}\exp\{-\beta n_k(\epsilon_k - \mu)\}}$$

for the total energy of the subsystem is $E = n_k\epsilon_k$ and the particle number is $N = n_k$. The $p(n_k)$ are partial probabilities (factors) of the $P\{n_k\}$ from Equation (12.17). In particular, we obtain

$$p_k^{\mathrm{MB}}(n_k) = \frac{\frac{1}{n_k!}\exp\{-\beta n_k(\epsilon_k - \mu)\}}{\sum_{n_k}\frac{1}{n_k!}\exp\{-\beta n_k(\epsilon_k - \mu)\}} = \frac{\frac{1}{n_k!}(z\exp\{-\beta\epsilon_k\})^{n_k}}{\exp\{z\exp\{-\beta\epsilon_k\}\}} \tag{12.53}$$

$$p_k^{\mathrm{BE}}(n_k) = \frac{\exp\{-\beta n_k(\epsilon_k - \mu)\}}{\sum_{n_k}\exp\{-\beta n_k(\epsilon_k - \mu)\}} = (z\exp\{-\beta\epsilon_k\})^{n_k}(1 - z\exp\{-\beta\epsilon_k\}) \tag{12.54}$$

Here we have exploited the fact that in the denominator of Equation (12.53) the power series expansion of an exponential function appears, while in the denominator of Equation (12.54) we have a geometric series. For fermions there exist only two probabilities at all, namely that to find one particle in $|k\rangle$, $(p_k(1))$, and that to find no particle, $(p_k(0))$:

$$p_k^{\mathrm{FD}}(1) = \frac{\exp\{-\beta(\epsilon_k - \mu)\}}{1 + \exp\{-\beta(\epsilon_k - \mu)\}} = \frac{1}{z^{-1}\exp\{\beta\epsilon_k\} + 1} \tag{12.55}$$

$$p_k^{\mathrm{FD}}(0) = \frac{1}{1 + \exp\{-\beta(\epsilon_k - \mu)\}} = \frac{1}{1 + z\exp\{-\beta\epsilon_k\}} \tag{12.56}$$

The distributions (12.53–56) are normalized:

$$\sum_{n_k} p_k(n_k) = 1$$

as one readily confirms. We now prove that Equation (12.48) is in fact the average of these distributions:

$$\begin{aligned}
\langle n_k \rangle^{\mathrm{MB}} &= \sum_{n_k=0}^{\infty} n_k p_k^{\mathrm{MB}}(n_k) \\
&= \frac{1}{\exp\{z\exp\{-\beta\epsilon_k\}\}} \sum_{n_k=0}^{\infty} n_k \frac{1}{n_k!} \left(\exp\{-\beta n_k(\epsilon_k - \mu)\}\right) \\
&= \frac{1}{\exp\{z\exp\{-\beta\epsilon_k\}\}} \left(-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k} \sum_{n_k=0}^{\infty} \frac{1}{n_k!} \exp\{-\beta n_k(\epsilon_k - \mu)\}\right)_{z,\beta} \\
&= \frac{1}{\exp\{z\exp\{-\beta\epsilon_k\}\}} \left(-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k} \exp\{z\exp\{-\beta\epsilon_k\}\}\right)_{z,\beta} \\
&= -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k} (z\exp\{-\beta\epsilon_k\})_{z,\beta} = z\exp\{-\beta\epsilon_k\}
\end{aligned} \tag{12.57}$$

This agrees exactly with Equation (12.48) for $a^{\mathrm{MB}} = 0$.

$$\begin{aligned}
\langle n_k \rangle^{\mathrm{BE}} &= \sum_{n_k=0}^{\infty} n_k p_k^{\mathrm{BE}}(n_k) \\
&= (1 - z\exp\{-\beta\epsilon_k\}) \sum_{n_k=0}^{\infty} n_k \exp\{-\beta n_k(\epsilon_k - \mu)\} \\
&= (1 - z\exp\{-\beta\epsilon_k\}) \left(-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k} \sum_{n_k=0}^{\infty} \exp\{-\beta n_k(\epsilon_k - \mu)\}\right)_{z,\beta} \\
&= (1 - z\exp\{-\beta\epsilon_k\}) \left(-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k} \frac{1}{1 - z\exp\{-\beta\epsilon_k\}}\right)_{z,\beta} \\
&= (1 - z\exp\{-\beta\epsilon_k\}) \frac{z\exp\{-\beta\epsilon_k\}}{(1 - z\exp\{-\beta\epsilon_k\})^2} = \frac{1}{z^{-1}\exp\{\beta\epsilon_k\} - 1}
\end{aligned} \tag{12.58}$$

For $a^{\mathrm{BE}} = -1$, Equation (12.58) becomes identical with Equation (12.48). Finally, in the case of Fermi-Dirac statistics, we have

$$\langle n_k \rangle^{\mathrm{FD}} = \sum_{n_k=0}^{1} n_k p_k^{\mathrm{FD}}(n_k) = p_k^{\mathrm{FD}}(1) = \frac{1}{z^{-1}\exp\{\beta\epsilon_k\} + 1} \tag{12.59}$$

With $a^{\mathrm{FD}} = +1$ Equation (12.59) is again identical with Equation (12.48). In this case even the following assertion holds: the probability $p_k^{\mathrm{FD}}(1)$, to find one fermion in the one-particle state $|k\rangle$, is identical with the average value of the occupation number of this level.

One obtains a better survey of the physical content of the distributions (12.53–56) if one expresses them in terms of their mean values:

$$p_k^{\mathrm{MB}}(n_k) = \frac{\left(\langle n_k \rangle^{\mathrm{MB}}\right)^{n_k}}{n_k!} \exp\left\{-\langle n_k \rangle^{\mathrm{MB}}\right\}$$

Here Equation (12.57) was simply inserted into (12.53). The distribution $p_k^{\mathrm{MB}}(n_k)$ is therefore a *Poisson distribution*, with the average $\langle n_k \rangle^{\mathrm{MB}}$. Inserting Equation (12.58) into (12.54) yields for the Bose-Einstein case, with

$$z \exp\{-\beta\epsilon_k\} = \left(\frac{1}{\langle n_k \rangle^{\mathrm{BE}}} + 1 \right)^{-1} = \left(\frac{\langle n_k \rangle^{\mathrm{BE}}}{\langle n_k \rangle^{\mathrm{BE}} + 1} \right)$$

the result

$$p_k^{\mathrm{BE}}(n_k) = \left(\frac{\langle n_k \rangle^{\mathrm{BE}}}{\langle n_k \rangle^{\mathrm{BE}} + 1} \right)^{n_k} \frac{1}{\langle n_k \rangle^{\mathrm{BE}} + 1} = \frac{\left(\langle n_k \rangle^{\mathrm{BE}} \right)^{n_k}}{\left(\langle n_k \rangle^{\mathrm{BE}} + 1 \right)^{n_k+1}}$$

i.e., a *geometric distribution*, with the average $\langle n_k \rangle^{\mathrm{BE}}$. Finally, for the Fermi-Dirac distribution it simply holds that

$$p_k^{\mathrm{FD}}(1) = \langle n_k \rangle^{\mathrm{FD}}$$
$$p_k^{\mathrm{FD}}(0) = 1 - p_k^{\mathrm{FD}}(1)$$

The Poisson distribution of the Maxwell–Boltzmann case expresses the fact that the particles statistically behave independently. For a Boltzmann particle, it does not matter which states the other particles occupy. In contrast, for bosons there exists a positive statistical correlation. The probability of finding a boson in a state which is already occupied by other bosons is larger, as predicted by the Boltzmann distribution. On the other hand, fermions possess a negative statistical correlation. If a state is already occupied, it is prohibited for other fermions because of Pauli's principle.

Example 12.2: Derivation of the mean occupation numbers

Because of the great importance of the mean occupation number $\langle n_k \rangle$ for quantum statistics we want to derive it again in another, very lucid way. To this end, we proceed quite similarly to the derivation of the canonical phase-space density at the beginning of Chapter 8. At first, we consider the one-particle energy spectrum.

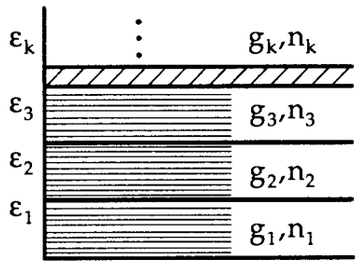


Figure 12.3. Combining one-particle energy levels to energy cells.

For macroscopic volumes the one-particle energy levels are very closely spaced, and even become continuous in the limit $V \to \infty$. Therefore, we divide the spectrum (see Figure 12.3) into energy cells ϵ_k, each of which contains g_k one-particle levels. In the limit of a single discrete level, g_k would be the degeneracy factor.

The energy cell ϵ_k with g_k different levels may contain n_k particles, and we ask for the most probable number n_k^* of particles in such a cell. The numbers n_k have to fulfill the conditions

$$N = \sum_k n_k$$
$$E = \sum_k n_k \epsilon_k \qquad \textbf{(12.60)}$$

We now consider how many ways exist to create a certain distribution $\{n_1, n_2, \ldots\}$. This will depend, of course, on whether the particles are distinguishable or not, and on how many particles can be put into a single level. Let us for the moment consider indistinguishable

fermions. There are exactly

$$w^{\mathrm{FD}}(n_k, g_k) = \binom{g_k}{n_k} = \frac{g_k!}{n_k!(g_k - n_k)!} \tag{12.61}$$

ways to distribute the n_k fermions over the g_k states in a certain cell, where it has to hold $g_k \geq n_k$, since each level can contain at most one fermion. The expression (12.61) is simply the number of ways of choosing n_k levels which are to be filled, from a set of g_k levels. The total number of all permutations for fermions is thus

$$w^{\mathrm{FD}}\{n_k\} = \prod_k \frac{g_k!}{n_k!(g_k - n_k)!}$$

For bosons, we have to distribute, quite analogously, n_k indistinguishable particles over the g_k states of the cell, but now, however, there is no restriction for the number of particles per energy level. We have already calculated in Example 8.1 the combinatoric factor belonging to this problem,

$$w^{\mathrm{BE}}(n_k, g_k) = \binom{n_k + g_k - 1}{n_k} = \frac{(n_k + g_k - 1)!}{n_k!(g_k - 1)!}$$

The total number of permutations is therefore

$$w^{\mathrm{BE}}\{n_k\} = \prod_k \frac{(n_k + g_k - 1)!}{n_k!(g_k - 1)!}$$

Finally, the Maxwell-Boltzmann case of distinguishable particles also shall be treated. We first assume that we have chosen a set of n_k fixed particle numbers for the energy cell ϵ_k. Then there are still g_k different permutations (energy levels) for each of these n_k particles, and thus

$$w^{\mathrm{MB}}(n_k, g_k) = g_k^{n_k} \tag{12.62}$$

However, to obtain the total number of all permutations, we must not only calculate the product of Equation (12.62) over all energy cells, but must also multiply by the number of ways of dividing the N particle numbers into sets of $n_1, n_2, \ldots$ particle numbers. Now there are $N!$ permutations of the N particle numbers, and we take the first n_1, the next n_2, etc., to form the set of $\{n_1, n_2, \ldots\}$ particle numbers for the energy cells. However, all $n_1!$ permutations among the first n_1 particles do not change the numbers in the energy cell ϵ_1, all $n_2!$ permutations of the next n_2 particles do not change the numbers in energy cell ϵ_2, etc. Thus, there are $N!/n_1!n_2!\cdots$ ways to form sets of $n_1, n_2, \ldots$ different particles out of N enumerated particles. The total number of ways to distribute the N particles among the energy levels is thus

$$w^{\mathrm{MB}}\{n_k\} = \frac{N!}{n_1!n_2!\cdots} \prod_k g_k^{n_k} = N! \prod_k \frac{g_k^{n_k}}{n_k!}$$

The further procedure is now clear. We look for the distribution $\{n_k\}$ which provides the largest number of permutations; i.e., we determine the distribution $\{n_k\}$ for which $w\{n_k\}$ or, more conveniently, $\ln w\{n_k\}$ assumes a maximum under the constraints (12.60). To this end we vary $\ln w\{n_k\}$ with respect to the numbers n_k. We take the constraints (12.60) into account via two Lagrange multipliers α and β:

$$\delta \ln w\{n_k\} - \alpha \sum_k \delta n_k - \beta \sum_k \epsilon_k \, \delta n_k = 0 \tag{12.63}$$

To be able to perform the variations we assume n_k, $g_k \gg 1$ and use Stirling's formula $\ln n! \approx n \ln n - n$. Then we obtain

$$\ln w^{\mathrm{FD}}\{n_k\} = \sum_k [g_k \ln g_k - n_k \ln n_k - (g_k - n_k) \ln(g_k - n_k)]$$

$$= \sum_k \left[n_k \ln\left(\frac{g_k}{n_k} - 1\right) - g_k \ln\left(1 - \frac{n_k}{g_k}\right)\right] \tag{12.64}$$

$$\ln w^{\mathrm{BE}}\{n_k\} = \sum_k [(n_k + g_k - 1) \ln(n_k + g_k - 1) - n_k \ln n_k - (g_k - 1) \ln(g_k - 1)]$$

$$\approx \sum_k \left[n_k \ln\left(\frac{g_k}{n_k} + 1\right) + g_k \ln\left(1 + \frac{n_k}{g_k}\right)\right] \tag{12.65}$$

Here we assumed that $g_k - 1 \approx g_k$ in the last step. We also obtain

$$\ln w^{\mathrm{MB}}\{n_k\} = \ln N! + \sum_k [n_k \ln g_k - n_k \ln n_k + n_k] \tag{12.66}$$

In Equation (12.66), the first term is constant and does not contribute to the variation. Therefore, we may also use the following instead of Equation (12.66):

$$\ln w^{\mathrm{MB}}\{n_k\} = \sum_k \left(n_k \ln \frac{g_k}{n_k} + n_k \right) \tag{12.67}$$

This has the advantage that for the following we can again evaluate all three cases in a unified form. Equations (12.64), (12.65), and (12.67) may be combined with the help of the symbol a from Equation (12.38) to yield one equation:

$$\ln w\{n_k\} = \sum_k \left[n_k \ln\left(\frac{g_k}{n_k} - a\right) - \frac{g_k}{a} \ln\left(1 - a\frac{n_k}{g_k}\right)\right] \tag{12.68}$$

For $a = +1$ we obtain the Fermi-Dirac case, for $a = -1$ the Bose-Einstein case, and for $a = 0$ the Maxwell-Boltzmann case. If we perform the variation (12.63) with (12.68), we obtain

$$\sum_k \left[\ln\left(\frac{g_k}{n_k} - a\right) - \alpha - \beta\epsilon_k \right]_{n_k = n_k^*} \delta n_k = 0 \tag{12.69}$$

Since we have taken into account the two constraints via two Lagrange multipliers, we may assume that here the variations δn_k are mutually independent. Then each coefficient in Equation (12.69) must vanish:

$$\ln\left(\frac{g_k}{n_k^*} - a\right) - \alpha - \beta\epsilon_k = 0$$

The most probable distribution of the N particles over the single states has thus the form

$$n_k^* = \frac{g_k}{\exp\{\alpha + \beta\epsilon_k\} + a} \tag{12.70}$$

The ratio n_k^*/g_k can now be interpreted as the most probable number of particles per energy level. The Lagrange multipliers α and β still have to be determined from the condition

$$N = \sum_k \frac{g_k}{\exp\{\alpha + \beta\epsilon_k\} + a}$$

$$E = \sum_k \frac{g_k \epsilon_k}{\exp\{\alpha + \beta\epsilon_k\} + a} \tag{12.71}$$

where we have to note that the sum does not run over single energy levels, but over the energy cells with g_k levels per cell. If one considers this, one observes that the formulas (12.70) and (12.71) are completely equivalent to Equations (12.48), (12.39), and (12.40).

13 The Ideal Bose Gas

As a first concrete application of quantum statistics we want to calculate in this section the properties of an ideal gas of (nonrelativistic) indistinguishable bosons. One has to expect that the ideal Bose gas becomes the ideal Boltzmann gas (classical ideal gas) at high temperatures and low densities. The largest deviations in thermodynamic properties should therefore occur if the condition

$$n\lambda^3 \equiv \frac{N}{V}\lambda^3 = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} \ll 1 \tag{13.1}$$

is no longer fulfilled. In applications to real systems, however, the parameter $n\lambda^3$ must not become too large, since for very small temperatures (small mean kinetic energy per particle) as well as for high densities (small mean distance between particles) the interactions in real systems are no longer negligible. The ideal Bose gas is thus a model system, where the influence of quantum effects can be very well studied, but which can only approximately describe real systems. Our aim now is to calculate the grand canonical partition function, or more simply, its logarithm (cf. Equation (12.37))

$$q(T, V, z) = \ln \mathcal{Z}(T, V, z) = -\sum_k \ln(1 - z\exp\{-\beta\epsilon_k\}) \tag{13.2}$$

for which we use the abbreviation $q(T, V, z)$. The one-particle energies ϵ_k are those of free quantum mechanical particles in a box of volume V (cf. Example 10.2). Since the chemical potential μ or the fugacity z, respectively, is not fixed for such a system, but the particle number is, z has to be determined from the equation (cf. Equation (12.39))

$$N = \sum_k \langle n_k\rangle^{\mathrm{BE}} = \sum_k \frac{1}{z^{-1}\exp\{\beta\epsilon_k\} - 1} \tag{13.3}$$

From this one can immediately draw an important conclusion. It must always hold that $0 \leq \langle n_k\rangle \leq N$ for all one-particle states $|k\rangle$; i.e., $z^{-1}\exp\{\beta\epsilon_k\} = \exp\{\beta(\epsilon_k - \mu)\} > 1$; thus $\epsilon_k > \mu$ for all k. The chemical potential of an ideal Bose gas must be smaller than the energy of the lowest one-particle level $\epsilon = 0$; i.e. $\mu \leq 0$ and $0 \leq z \leq 1$. This is equivalent to the fact that bosons seem to feel an attractive potential, and that adding further bosons to

the system costs no energy. The restriction of the fugacity to the interval $0 \leq z \leq 1$ is very important in the following. For a large volume, the sum over all one-particle states can be rewritten in terms of an integral,

$$\sum_k \to \frac{V}{(2\pi)^3} \int d^3k = \frac{2\pi V}{h^3} (2m)^{3/2} \int \epsilon^{1/2}\, d\epsilon \tag{13.4}$$

For the last transformation we have used $\epsilon_k = \hbar^2 \vec{k}^2/(2m)$. This formulation can also be derived by considering the classical phase space. The quantity

$$\Sigma = \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} = \frac{4\pi V}{h^3} \int p^2\, dp = \frac{2\pi V}{h^3} (2m)^{3/2} \int \epsilon^{1/2}\, d\epsilon \tag{13.5}$$

is the number of states in the one-particle phase space, and

$$g(\epsilon) = \frac{d\Sigma}{d\epsilon} = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} \tag{13.6}$$

is to be interpreted as the *one-particle density of states*. This yields exactly the above replacement $\sum_k \to \int g(\epsilon)\, d\epsilon$. Therewith, the sums in Equations (13.2) and (13.3) can be rewritten in terms of integrals. However, a detail must be taken into account. As long as a large, but finite volume is given, the one-particle states are very close to each other but still not continuous. In this case, the approximation by an integral is very bad for small energies $\epsilon \to 0$. Namely, in a box with periodic boundary conditions there exists a state having $\epsilon = 0$, with the one-particle wavefunction $\phi_0(\vec{r}) = V^{-1/2}$. However, in the integral approximation this state does not appear, since $g(0) = 0$. On first sight, this does not seem to be of any importance, since all other states are very well approximated. However, we will soon see that the state $\epsilon = 0$ plays a special role in the Bose gas. We therefore have to explicitly account for the term for $k = 0$ ($\epsilon = 0$) in the sums (13.2) and (13.3):

$$\begin{aligned} q(T, V, z) &= -\frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \epsilon^{1/2}\, d\epsilon \ln(1 - z \exp\{-\beta\epsilon\}) - \ln(1 - z) \\ &= \frac{2\pi V}{h^3} (2m)^{3/2} \frac{2}{3} \beta \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{z^{-1} \exp\{\beta\epsilon\} - 1} - \ln(1 - z) \end{aligned} \tag{13.7}$$

Here we have performed an integration by parts between the first and second lines. The last term in Equation (13.7) is just Equation (13.2) evaluated for $\epsilon = 0$. Equation (13.3) determines the particle number, which reads

$$N(T, V, z) = \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty d\epsilon \frac{\epsilon^{1/2}}{z^{-1} \exp\{\beta\epsilon\} - 1} + \frac{z}{1 - z} \tag{13.8}$$

Also, here the last term, $N_0 = z/(1 - z)$, represents the contribution of the level $\epsilon = 0$ to the total (mean) particle number (13.3) and thus gives the number of particles in this state.

The integrals occurring in Equations (13.7) and (13.8) are standard integrals of mathematical physics. They can be transformed by the substitution $x = \beta\epsilon$ into the general form

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}\, dx}{z^{-1} \exp\{x\} - 1} \qquad 0 \leq z \leq 1, \quad n \in R \tag{13.9}$$

where $\Gamma(n)$ is the Gamma function. Thus Equations (13.7) and (13.8) become

$$q(T, V, z) = \frac{V}{\lambda^3} g_{5/2}(z) - \ln(1 - z) \tag{13.10}$$

$$N(T, V, z) = \frac{V}{\lambda^3} g_{3/2}(z) + N_0(z) \tag{13.11}$$

Our aim now is to determine the fugacity z of the gas from Equation (13.11) (for given particle number), and afterwards to insert it into Equation (13.10). Unfortunately, this cannot be done explicitly, since the functions $g_n(z)$ are defined by the integral (13.9), and do not possess a representation in terms of "simple" functions. Therefore, we will first try to make a survey of the properties of the $g_n(z)$. To this end, we expand the integrand ($z \exp\{-x\} = \exp\{-\beta(\epsilon - \mu)\} \leq 1$):

$$\begin{aligned} \frac{1}{z^{-1} \exp\{x\} - 1} &= z \exp\{-x\} \frac{1}{1 - z \exp\{-x\}} \\ &= z \exp\{-x\} \sum_{k=0}^{\infty} (z \exp\{-x\})^k \\ &= \sum_{k=1}^{\infty} z^k \exp\{-kx\} \end{aligned} \tag{13.12}$$

This leads to

$$\begin{aligned} g_n(z) &= \frac{1}{\Gamma(n)} \sum_{k=1}^{\infty} z^k \int_0^{\infty} x^{n-1} \exp\{-kx\}\, dx \\ &= \frac{1}{\Gamma(n)} \sum_{k=1}^{\infty} \frac{z^k}{k^n} \int_0^{\infty} y^{n-1} \exp\{-y\}\, dy \end{aligned} \tag{13.13}$$

The last integral is simply $\Gamma(n)$, and thus

$$g_n(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^n} \qquad 0 \leq z \leq 1 \tag{13.14}$$

Equation (13.14) provides an interesting relationship to Riemann's Zeta function $\zeta(n)$. For $z = 1$ ($\mu = 0$), we have

$$g_n(1) = \sum_{k=1}^{\infty} \frac{1}{k^n} = \zeta(n) \qquad n > 1 \tag{13.15}$$

This series converges only for $n > 1$, which, however, does not mean that the functions $g_n(z)$ are defined only for $n > 1$, but that $g_n(z) \to \infty$ for $n \leq 1$ and $z \to 1$; on the other hand $g_n(z)$ is finite for $n > 1$ for all $0 \leq z \leq 1$. Some special values of the often used

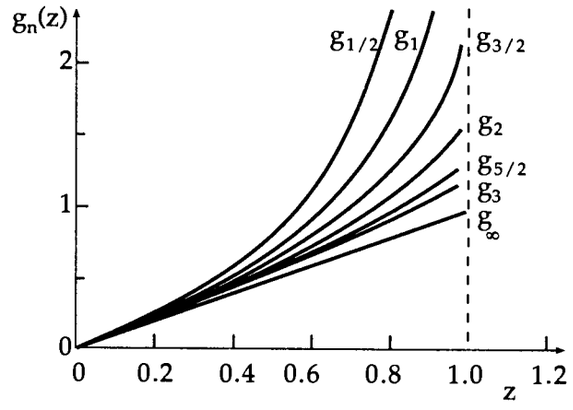


Figure 13.1. The functions $g_n(z)$.

ζ-function may be stated here:

$$\begin{array}{lll} \zeta(1) \to \infty & \zeta(3/2) \approx 2.612 & \zeta(2) = \pi^2/6 \approx 1.645 \\ \zeta(5/2) \approx 1.341 & \zeta(3) \approx 1.202 & \zeta(7/2) \approx 1.127 \\ \zeta(4) = \pi^4/90 \approx 1.082 & \zeta(6) = \pi^6/945 \approx 1.017 & \zeta(8) = \pi^8/9450 \approx 1.004 \end{array} \tag{13.16}$$

Now we already have a good feeling of the shape of the $g_n(z)$. They all start at the origin ($z = 0$) with slope 1 and diverge for $z \to 1$, if $n \leq 1$ (see Figure 13.1). For $n > 1$ they have a finite value at $z = 1$, which, as one sees from Equations (13.16) becomes steadily smaller with increasing n. For $n \to \infty$, $g_n(z) \approx z$. Since the series (13.15) converges only very slowly for $z = 1$ and small n, in practice the integrals (13.7) and (13.8) are most conveniently calculated on a computer.

We now want to investigate the physical properties of the Bose gas in greater detail. We start from Equation (13.11), from which we have to determine the fugacity z for given N, V, and T:

$$N = \frac{V}{\lambda^3} g_{3/2}(z) + \frac{z}{1-z} = N_\epsilon + N_0 \tag{13.17}$$

The first term N_ϵ represents the number of particles in excited states, while N_0 determines the number of particles in the state $\epsilon = 0$. We first consider the order of magnitude of the terms. Of course, $N \gg 1$, and for temperatures which are not too small, in general $V\lambda^{-3} \gg 1$. On the other hand, $g_{3/2}$ is restricted to the range $0 \leq g_{3/2}(z) \leq \zeta(3/2) = 2.612$. For a given V and T the first term in Equation (13.17) can at most assume the value

$$N_\epsilon^{\max} = \frac{V}{\lambda^3}\zeta(3/2) = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\zeta(3/2) \propto VT^{3/2} \tag{13.18}$$

Thus, no more than $N_\epsilon^{\max}$ particles can be in excited states. On the other hand, the term $N_0 = z/(1-z)$ can be neglected as long as z is not very close to one. If N_0 is to contribute noticeably to the particle number, it has to hold that

$$N \approx N_0 = \frac{z}{1-z} \quad \text{or} \quad z \approx \frac{N}{N+1} \approx 1 \tag{13.19}$$

We now study the thermodynamic limit of Equation (13.17) ($N \to \infty$, $V \to \infty$, $N/V =$ const.). To this end we write Equation (13.17) in the form

$$1 = \frac{N_\epsilon}{N} + \frac{N_0}{N} \qquad N_\epsilon = \frac{V}{\lambda^3} g_{3/2}(z) \qquad N_0 = \frac{z}{1-z} \tag{13.20}$$

In the thermodynamic limit we now have to distinguish between two cases. For $z \neq 1$, N_0 is finite and $N_0/N \to 0$. The number of particles in the ground state is then negligibly small: all particles occupy excited states. If $z = 1$, $N_\epsilon = N_\epsilon^{\max}$. In principle, N_0 is then divergent, and N_0/N is an indeterminate expression. In this case, N_0 is given by the excess $N - N_\epsilon^{\max}$. The excited states no longer contain all particles, and it becomes favorable for the system to fill the state $\epsilon = 0$ with the excess particles. In summary, we obtain:

$$1 = \frac{N_\epsilon}{N} + \frac{N_0}{N} \lim_{N\to\infty} \begin{cases} 1 = \dfrac{N_\epsilon}{N}, \ \dfrac{N_0}{N} = 0 & \text{for } z < 1 \\ 1 = \dfrac{N_\epsilon^{\max}}{N} + \dfrac{N_0}{N} & \text{for } z = 1 \end{cases} \tag{13.21}$$

We now want to investigate this phenomenon, which is called *Bose condensation*, in somewhat greater detail. We fix the independent variables N, V, and T of the system. If it holds that

$$N < N_\epsilon^{\max} = \frac{V}{\lambda^3} \zeta\left(\frac{3}{2}\right) \qquad \text{or} \qquad \frac{N\lambda^3}{V} < \zeta\left(\frac{3}{2}\right) \tag{13.22}$$

all N particles can be placed in excited states. The fugacity is different from unity ($z < 1$), and has to be determined from the equation

$$N = \frac{V}{\lambda^3} g_{3/2}(z) \tag{13.23}$$

In this case, the second term, N_0, in Equations (13.11) or (13.17), can be neglected. However, if now

$$N > N_\epsilon^{\max} = \frac{V}{\lambda^3} \zeta\left(\frac{3}{2}\right) \tag{13.24}$$

the excited states ($\epsilon > 0$) are not enough to contain all of the particles. Then $z = 1$, and the excess

$$N_0 = N - N_\epsilon^{\max} = N - \frac{V}{\lambda^3} \zeta\left(\frac{3}{2}\right) \tag{13.25}$$

condenses in the ground state $\epsilon = 0$. The transformation between Equations (13.22) and (13.24) happens just when

$$\frac{N\lambda^3}{V} = \zeta\left(\frac{3}{2}\right) \tag{13.26}$$

For large temperatures and low densities, we have the case of Equation (13.22). The thermal energy is sufficiently large to excite (nearly) all particles into higher levels $\epsilon > 0$. On the contrary, if the temperature becomes very small or the density sufficiently high, the positive

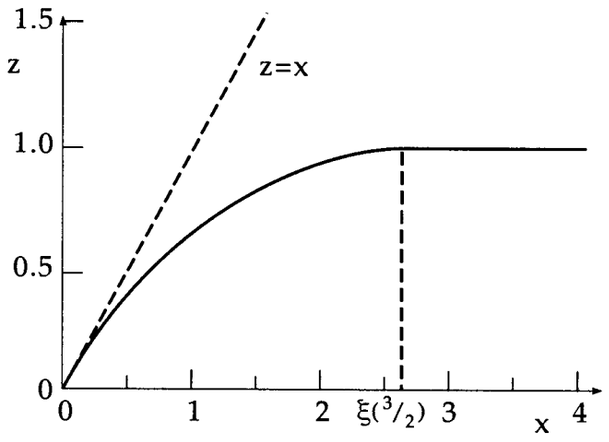


Figure 13.2. $z(x)$, according to Equation (13.28).

statistical correlation of the bosons becomes strongly noticeable. The bosons try to gather in the state $\epsilon = 0$. It becomes favorable (more probable) for the system to no longer distribute the thermal excitation energy homogeneously over all particles, but only over the fraction $N_\epsilon^{\max}/N$, and to put the rest, N_0, into the ground state $\epsilon = 0$. We have already noticed when discussing the occupation number distribution that the probability of finding many bosons in the same state is larger than in the classical case. At large temperatures, however, this is not very obvious, since then the excitation energy is sufficient to distribute the particles over many different states. If we introduce the parameter x via

$$x = \frac{N\lambda^3}{V} \tag{13.27}$$

we obtain for the fugacity, from Equation (13.23),

$$z = \begin{cases} 1 & \text{if } x \geq \zeta(3/2) \\ \text{solution of } x = g_{3/2}(z) & \text{if } x < \zeta(3/2) \end{cases} \tag{13.28}$$

If one evaluates Equation (13.28) numerically, the following picture results: the curve $z(x)$ has a kink at $x = \zeta(3/2)$ (see Figure 13.2). This, however, holds only in the thermodynamic limit. For finite particle numbers ($N \gg 1$), the kink is smoothened, since z then has to be numerically determined from the full Equation (13.17), whereby N_0/N can no longer be neglected compared to N_ϵ/N. Then everywhere $z < 1$.

Bose condensation does not set in spontaneously at $x = \zeta(3/2)$, but one always has $N_0 > 0$ and $N_\epsilon < N_\epsilon^{\max}$. For very small values of $x (= g_{3/2}(z))$ ($x \ll 1$), $g_{3/2}(z)$ converges and is essentially given by the first terms of the expansion (13.14),

$$x = z + \frac{z^2}{2^{3/2}} + \cdots \qquad \text{if} \qquad x \ll 1 \qquad \text{or} \qquad z \approx x = \frac{N\lambda^3}{V} \tag{13.29}$$

This is just the limit of the classical ideal gas, as one obtains from a comparison with Equation (9.46) (dashed line in Figure 13.2). For the particle numbers N_ϵ and N_0 one

obtains, using Equations (13.28) and (13.21):

$$N_\epsilon = \begin{cases} N & \text{if } x < \zeta(3/2) \text{ i.e., } N < N_\epsilon^{\max} \\ N_\epsilon^{\max} & \text{if } x \geq \zeta(3/2) \text{ i.e., } N \geq N_\epsilon^{\max} \end{cases} \tag{13.30}$$

$$N_0 = \begin{cases} 0 & \text{if } x < \zeta(3/2) \\ N - N_\epsilon^{\max} & \text{if } x \geq \zeta(3/2) \end{cases} \tag{13.31}$$

Let us now consider an ideal Bose gas at given particle density N/V as a function of temperature. Then Equation (13.26) defines a critical temperature T_c, below which Bose condensation sets in:

$$kT_c = \left(\frac{N}{V}\right)^{2/3} \frac{h^2}{2\pi m(\zeta(3/2))^{2/3}} \tag{13.32}$$

If one expresses $N_\epsilon^{\max}$ in Equation (13.18) in terms of the critical temperature, Equations (13.30) and (13.31) become

$$\frac{N_\epsilon}{N} = \begin{cases} 1 & T \geq T_c \\ \left(\frac{T}{T_c}\right)^{3/2} & T < T_c \end{cases} \tag{13.33}$$

$$\frac{N_0}{N} = \begin{cases} 0 & T \geq T_c \\ 1 - \left(\frac{T}{T_c}\right)^{3/2} & T < T_c \end{cases} \tag{13.34}$$

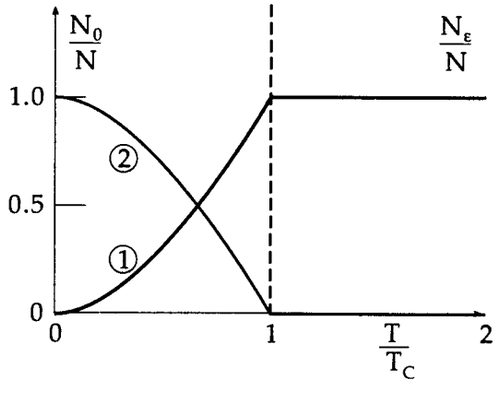


Figure 13.3. $N_\epsilon(T)/N$ and $N_0(T)/N$.

These functions are illustrated in Figure 13.3. One quickly realizes how, from $T = T_c$ on, the state $\epsilon = 0$ has to contain more and more particles as the system is further cooled down. However, this picture actually holds only in the thermodynamic limit, i.e., for $N \to \infty$. For finite particle numbers, no kinks occur at $T = T_c$.

Since the fugacity $z(T, V, N)$ is now known, we can also investigate the grand canonical potential or $q(T, V, z)$. Equation (13.32) yields $pV = kTq(T, V, z)$. Thus, according to Equation (13.10) it holds for the pressure that

$$p = \frac{kT}{\lambda^3} g_{5/2}(z) - \frac{kT}{V} \ln(1 - z) \tag{13.35}$$

Here it is also convenient to first consider the thermodynamic limit ($N \to \infty$). One readily observes that the last term in Equation (13.35) can be always neglected. If $z < 1$, $\ln(1 - z)$ is finite and this term goes to zero for $V \to \infty$. Furthermore, $1 - z$ can at most decrease as $1/(N + 1)$ according to Equation (13.20), so that the product of V^{-1} with the logarithmically divergent term $\ln(N + 1)$ vanishes for $N \to \infty$ and $V \to \infty$ ($N/V = \text{const.}$). This simply means that the particles in the ground state $\epsilon = 0$, having

no kinetic energy, do not contribute to the pressure, which is obvious; i.e.,

$$p = \frac{kT}{\lambda^3} g_{5/2}(z) \tag{13.36}$$

Below the critical temperature ($T < T_c$) we may set $z = 1$. In this region, the pressure

$$p = \frac{kT}{\lambda^3} \zeta(5/2) \tag{13.37}$$

becomes independent of volume and particle number, and is solely a function of temperature. This is, of course, also a consequence of the fact that the particles in the ground state do not contribute to the pressure. If, for instance, one adds additional particles to the system at given temperature $T < T_c$, they would sit necessarily in the state $\epsilon = 0$ and would not contribute to the pressure. A similar consideration holds if the volume decreases. This would also have the only consequence that more particles would condense in the state $\epsilon = 0$, but would not effect an increase in pressure. Just as Equation (13.26) defines a critical temperature T_c at given density, this equation yields a critical density at given temperature (or if the particle number is given as well, a critical volume), above which Bose condensation sets in:

$$\left(\frac{N}{V}\right)_c = \frac{\zeta(3/2)}{\lambda^3} \qquad \text{or} \qquad V_c = \frac{N\lambda^3}{\zeta(3/2)} \tag{13.38}$$

From Equations (13.37) and (13.38) one concludes that the isotherms of the Bose gas are horizontal lines in the pV diagram for volumes $V < V_c$, just like a van der Waals gas in the coexistence region of gas and liquid. One therefore interprets Bose condensation as a kind of phase transition in such a system. One phase is represented by the particles in the excited states, while the other phase is formed by the particles in the state $\epsilon = 0$. However, Bose condensation is not a condensation in coordinate space, as in the phase transition gas–liquid, but a condensation in momentum space, in which particles gather in a certain momentum state.

If one eliminates the temperature from Equations (13.37) and (13.38), one obtains the limiting curve in the pV diagram where Bose condensation sets in:

$$pV_c^{5/3} = \text{const.} = \frac{h^2}{2\pi m} \frac{\zeta(5/2)}{(\zeta(3/2))^{5/3}} N^{5/3} \tag{13.39}$$

In the regions $T > T_c$ or $V > V_c$, respectively, one obtains with the help of Equation (13.29), for $x \ll 1$, the classical limit of an ideal gas. Then one may approximate the function $g_{5/2}(z)$ in Equation (13.36) by the first terms of the series (13.14):

$$p = \frac{kT}{\lambda^3} \left(z + \frac{z^2}{2^{5/2}} + \cdots\right) \tag{13.40}$$

If one restricts oneself here, as in Equation (13.29), to the first term, the ideal gas law follows ($x \approx z \ll 1$):

$$p = \frac{kT}{\lambda^3} z = \frac{kT}{\lambda^3} x = \frac{NkT}{V} \tag{13.41}$$

If one also takes into account also higher order terms, one can successively eliminate the fugacity z from the expansions (13.29) and (13.40). This leads to a systematic expansion of the pressure in terms of the parameter x:

$$\frac{pV}{NkT} = \sum_{l=1}^{\infty} a_l x^{l-1} \qquad x = \frac{N\lambda^3}{V} \tag{13.42}$$

The first coefficients of this virial expansion of the Bose gas read

$$\begin{aligned} a_1 &= 1 \\ a_2 &= -\frac{1}{4\sqrt{2}} \\ a_3 &= -\left(\frac{2}{9\sqrt{3}} - \frac{1}{8}\right) \end{aligned} \tag{13.43}$$

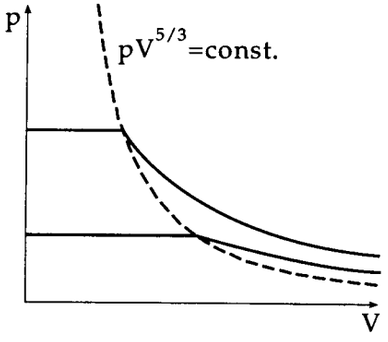


Figure 13.4. Isotherms of the ideal Bose gas.

In Figure 13.4 the isotherms of the Bose gas are depicted as they can be calculated from Equations (13.40) or (13.37). The dashed curve, Equation (13.39), represents the onset of the phase transition.

Finally, we want to consider the internal energy U and the specific heat of the Bose gas:

$$U = -\left.\frac{\partial}{\partial\beta} \ln \mathcal{Z}\right|_{z,V} = \frac{3}{2} kT \frac{V}{\lambda^3} g_{5/2}(z) \tag{13.44}$$

Comparison with Equation (13.36) yields

$$p = \frac{2}{3}\frac{U}{V} \tag{13.45}$$

independent of whether the system is in a one- or two-phase region. This relation is already well known to us from the ideal gas. With the pressure we thus also know the energy density of the system.

To calculate the specific heat at constant volume C_V, we proceed as follows:

$$U = \frac{3}{2} pV = \frac{3}{2} kT \frac{V}{\lambda^3} g_{5/2}(z) \tag{13.46}$$

For $T < T_c$ we have $z = 1$, independent of temperature, so that

$$\begin{aligned} \frac{C_V}{Nk} &= \frac{1}{Nk} \left.\frac{\partial U}{\partial T}\right|_{N,V} \\ &= \frac{3}{2}\frac{V}{N} \zeta(5/2) \frac{\partial}{\partial T}\left(\frac{T}{\lambda^3}\right) \\ &= \frac{15}{4} \zeta(5/2) \frac{V}{N\lambda^3} \propto T^{3/2} \end{aligned} \tag{13.47}$$

For $T > T_c$, z is no longer independent of T. However, since now $N_0 \approx 0$, we can eliminate the term $V\lambda^{-3}$ in Equation (13.46) with the help of Equation (13.23):

$$U = \frac{3}{2} NkT \frac{g_{5/2}(z)}{g_{3/2}(z)} \tag{13.48}$$

One readily recognizes the classical limit for $z \ll 1$. For the specific heat, one obtains

$$\begin{aligned} \frac{C_V}{Nk} &= \frac{1}{Nk} \left.\frac{\partial U}{\partial T}\right|_{N,V} \\ &= \frac{3}{2} \frac{g_{5/2}(z)}{g_{3/2}(z)} + \frac{3}{2} T \left.\frac{\partial}{\partial T} \left(\frac{g_{5/2}(z)}{g_{3/2}(z)} \right)\right|_{N,V} \end{aligned} \tag{13.49}$$

In Equation (13.49), the derivative of the $g_n(z)$ with respect to their arguments is required (chain rule). Employing the series expansion (13.14), one immediately anticipates the following recursion relation:

$$g_n'(z) = \frac{1}{z} g_{n-1}(z) \tag{13.50}$$

With this one obtains

$$\frac{\partial}{\partial T} \left(\frac{g_{5/2}(z)}{g_{3/2}(z)} \right) = \frac{\partial z}{\partial T} \frac{1}{z} \left(1 - \frac{g_{5/2}(z) g_{1/2}(z)}{(g_{3/2}(z))^2} \right) \tag{13.51}$$

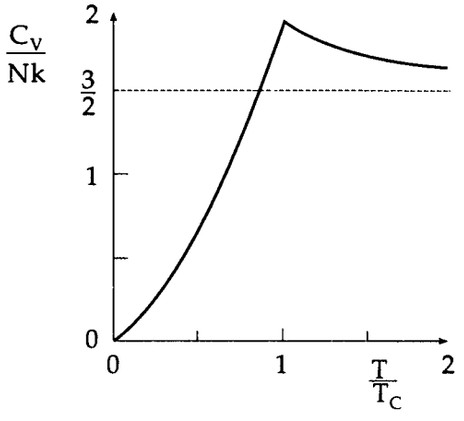


Figure 13.5. Specific heat of the ideal Bose gas.

The expression $\partial z/\partial T$ can be determined from Equation (13.23) as follows:

$$\begin{aligned} &\frac{\partial}{\partial T} g_{3/2}(z) = \frac{\partial}{\partial T} \left(\frac{N\lambda^3}{V} \right) \\ &\frac{\partial z}{\partial T} \frac{1}{z} g_{1/2}(z) = -\frac{3}{2T} \left(\frac{N\lambda^3}{V} \right) = -\frac{3}{2T} g_{3/2}(z) \\ &\frac{\partial z}{\partial T} = -\frac{3z}{2T} \frac{g_{3/2}(z)}{g_{1/2}(z)} \end{aligned} \tag{13.52}$$

If one inserts this, with Equation (13.51), into Equation (13.49), one obtains

$$\frac{C_V}{Nk} = \frac{15}{4} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)} \qquad T > T_c \tag{13.53}$$

The classical limit ($z \to 0$) can be easily read off; it holds that $C_V = \left(\frac{15}{4} - \frac{9}{4}\right) Nk = \frac{3}{2} Nk$ (ideal gas). For $z \to 1$ ($T \to T_c$), $g_{1/2}$ is divergent, and the second term in Equation (13.53) vanishes, so that Equation (13.53) becomes identical to Equation (13.47), with $g_{3/2}(z) = x = N\lambda^3/V$. Then the specific heat has the value

$$C_V(T_c) = \frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)} Nk = 1.925 Nk > C_V^{\text{ideal}} \tag{13.54}$$

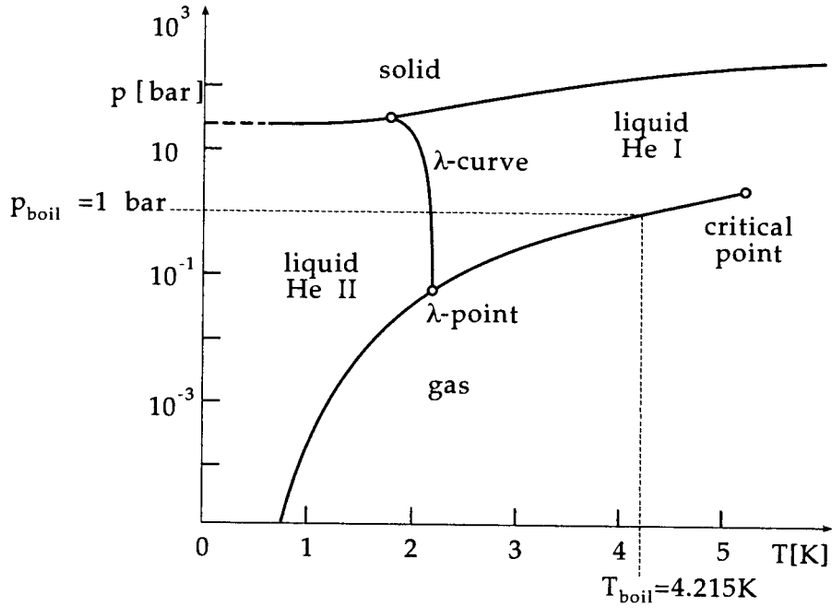


Figure 13.6. Phase diagram of ^{4}He.

at the critical temperature T_c. With Equations (13.53) and (13.47) one consequently obtains the following picture of the specific heat, which is depicted in Figure 13.5: in the region of Bose condensation, $T/T_c < 1$, the specific heat increases like $T^{3/2}$ to the maximum value, Equation (13.54). At $T = T_c$ a spike appears, and for $T \to \infty$, C_V approaches the value of the ideal gas.

The appearance of a spike in the specific heat is typical for a *second-order phase transition* (no latent heat). A kink appears in the first derivative of the thermodynamic potential U, and a discontinuity appears in the second derivative $\partial C_V/\partial T = \partial^2 U/\partial T^2$.

Example 13.1: λ-point in ^{4}He

The specific heat of ^{4}He for example shows such a behavior at very low temperatures. By 1938 F. London already had surmised that Bose-Einstein condensation might be responsible for this peculiar behavior.

For the critical temperature of Bose-condensation one finds from Equation (13.32), with $m = 6.65 \cdot 10^{-24}$ g and $v = 2.76 \cdot 10^{-5}$ m^{3}mol^{-1}, $T_c = 3.13$ K, which is at least in the vicinity of the measured value. However, the experimentally found spike is by far sharper. It has the shape of the greek letter λ, which is the reason for introducing the name λ-point for the critical temperature in ^{4}He. For a quantitative explanation, however, one has also to take into account the interaction of the ^{4}He particles. The phase diagram of ^{4}He is shown in Figure 13.6, and its specific heat is shown in Figure 13.7.

Below the (slightly pressure-dependent) critical temperature (λ-curve), liquid helium suddenly shows very interesting new properties. From the horizontal limiting curve solid–liquid for $T \to 0$, one concludes with the help of the Clausius-Clapeyron equation,

$$\frac{dp}{dT} = 0 = \frac{s_{fl} - s_{\text{solid}}}{v_{fl} - v_{\text{solid}}} \qquad (13.55)$$

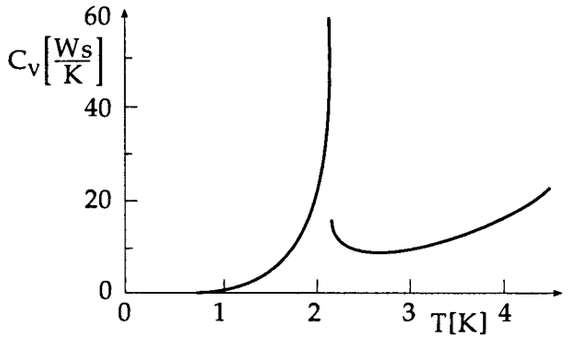


Figure 13.7. Specific heat of ^{4}He.

that liquid He II (for $T \to 0$) has no more entropy per mole than solid helium. The condensation of the particles in the state $\epsilon = 0$ already represents the form of He with the highest degree of order. Furthermore, the viscosity of He II can assume very small values (depending on the experimental conditions). Liquid He II may then permeate very narrow capillaries, and even porous vessels, out of which not even gaseous He could escape. One interprets He II as a mixture of two phases, the superfluid He (particles in the state $\epsilon = 0$, entropy $S = 0$) and normal fluid helium. A further interesting property of He II is its very large heat conductivity. This leads, for instance, to the fact that He II does not boil below the λ-point (formation of bubbles), but evaporates from the surface steadily and calmly, since local temperature fluctuations cannot develop.

Ultrarelativistic Bose gas

Another interesting model system is an ideal gas of noninteracting bosons having a relativistic energy–momentum relationship and vanishing rest mass. A corresponding classical case was discussed in Example 6.2 and Exercise 7.2. The one-particle energies are

$$\epsilon_k = c\,|\vec{p}| = \hbar c\,\left|\vec{k}\right| \tag{13.56}$$

As in preceding sections (cf. Equations (13.2) and 12.37)), the grand canonical partition function for this system has to be calculated,

$$q(T, V, z) = \ln \mathcal{Z} = -\sum_k \ln(1 - z\exp\{-\beta\epsilon_k\}) \tag{13.57}$$

For the mean particle number and the internal energy we have the equations (cf. Equations (13.3) and (12.39))

$$N(T, V, z) = \sum_k \frac{1}{z^{-1}\exp\{\beta\epsilon_k\} - 1} \tag{13.58}$$

$$U(T, V, z) = \sum_k \frac{\epsilon_k}{z^{-1}\exp\{\beta\epsilon_k\} - 1} \tag{13.59}$$

In principle, the vectors $\vec{k}$ are discrete in a box having periodic boundary conditions (Example 10.2). For large volumes, however, we can again rewrite the sums in Equations (13.57–59) in terms of integrals. To this end, we proceed exactly as in Equations (13.5) and (13.6). The total number of states in the (classical) phase space is

$$\Sigma = \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} = \frac{4\pi V}{h^3} \int_0^\infty p^2\, dp = \frac{4\pi V}{h^3 c^3} \int_0^\infty \epsilon^2\, d\epsilon \tag{13.60}$$

with the one-particle density of states

$$g(\epsilon) = \frac{\partial \Sigma}{\partial \epsilon} = \frac{4\pi V}{h^3 c^3} \epsilon^2 \tag{13.61}$$

The density of states has changed, compared to the nonrelativistic case, due to the other energy–momentum relation.

The ultrarelativistic Bose gas, however, requires yet another consideration with respect to the chemical potential. In the relativistic case, it is possible to create a particle of rest mass m_0 if at least the energy $E = m_0 c^2$ is spent (or, with $2m_0c^2$, a particle and an antiparticle). However, since the ultrarelativistic particles have no rest mass, it is possible to create arbitrarily many of these particles having $\epsilon_k = 0$ without energy cost; i.e., in the state $\epsilon = 0$ there may be, in principle, arbitrarily many particles. Therefore, it makes no sense to fix the number of ultrarelativistic particles, since it may become arbitrarily large. Thus, the chemical potential μ also must have the value 0 ($\mu = 0$, $z = 1$), since it costs no energy to add arbitrarily many particles to the system in the state $\epsilon = 0$. This divergence of the occupation number $\langle n_0 \rangle$ in the state $\epsilon = 0$ has, of course, no effect on the essential physical properties like pressure, internal energy, etc., since the particles having $\epsilon = 0$ do not contribute to them at all.

Thus, we are freed of a large part of the difficulties of the last section, since z has here simply the constant value $z = 1$:

$$\begin{aligned} q(T, V) &= -\frac{4\pi V}{(hc)^3} \int_0^\infty d\epsilon \epsilon^2 \ln(1 - \exp\{-\beta\epsilon\}) \\ &= \frac{4\pi V}{(hc)^3} \frac{1}{3} \beta \int_0^\infty d\epsilon \frac{\epsilon^3}{\exp\{\beta\epsilon\} - 1} \end{aligned} \tag{13.62}$$

Where an integration by parts was performed between the steps shown. For the internal energy, it follows from Equation (13.59) that

$$U(T, V) = \frac{4\pi V}{(hc)^3} \int_0^\infty d\epsilon \frac{\epsilon^3}{\exp\{\beta\epsilon\} - 1} \tag{13.63}$$

Because $q = pV/kT$, it follows from comparing Equations (13.62) and (13.63) that

$$p = \frac{1}{3} \left(\frac{U}{V} \right) \tag{13.64}$$

a relation which we have already found in the classical case in Example 6.2. Again there appears the factor 1/3, in contrast to the nonrelativistic case, where the pressure was 2/3 of the energy density.

With the substitution $x = \beta\epsilon$, the expressions in Equations (13.62) and (13.63) can be retraced to the standard integrals $g_n(z)$ from Equation (13.9), where now, of course, we simply have $z = 1$,

$$q(V, T) = \frac{pV}{kT} = \frac{4\pi V}{(hc)^3} \frac{2}{\beta^3} g_4(1) \tag{13.65}$$

With the values (13.16) one finds $g_4(1) = \zeta(4) = \pi^4/90$, and thus

$$p = \frac{1}{3} \frac{U}{V} = \frac{8\pi}{(hc)^3} (kT)^4 \frac{\pi^4}{90} \tag{13.66}$$

The pressure and the energy density are thus functions of the temperature alone, p, $U/V \propto T^4$, and the isotherms are horizontal in the pV diagram. Because $U = TS - pV + \mu N = TS - pV$ ($\mu = 0$), we can immediately calculate the free energy $F = U - TS = -pV$:

$$F = -pV = -\frac{1}{3} U = -\frac{8\pi^5}{90(hc)^3} V(kT)^4 \tag{13.67}$$

and the entropy as well, $S = \frac{1}{T}(U - F) = \frac{4}{3}\frac{U}{T}$:

$$S = \frac{32\pi^5}{90(hc)^3} (kT)^3 Vk \tag{13.68}$$

The entropy density is therefore $S/V \propto T^3$. Thus, the specific heat at constant volume becomes

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = 3S \tag{13.69}$$

i.e., it vanishes as T^3 for $T \to 0$. From Equations (13.66) and (13.68) we can finally find the adiabats ($S = \text{const.}$),

$$VT^3 = \text{const.} \qquad pT^{-4} = \text{const.} \qquad \Rightarrow pV^{4/3} = \text{const.} \tag{13.70}$$

so that $p \propto n^{4/3}$ with $n = N/V$. The mean particle number can be calculated from Equation (13.58),

$$N(V, T) = \frac{4\pi V}{(hc)^3} \int_0^\infty d\epsilon \frac{\epsilon^2}{\exp\{\beta\epsilon\} - 1} = \frac{8\pi V}{(hc)^3} \frac{1}{\beta^3} g_3(1) \tag{13.71}$$

Because $g_3(1) = \zeta(3)$ one obtains

$$N(V, T) = \frac{8\pi V}{(hc)^3} \zeta(3)(kT)^3 \tag{13.72}$$

The mean particle density thus increases like T^3. However, a comment is in order concerning Equation (13.72). First, the particle number (13.72) does not contain an infinite number of particles in the state $\epsilon = 0$, since their weight in the integral is zero ($g(0) = 0$). Second, we deal here only with the mean particle number, and one has to check how large the fluctuations around this number are. The standard deviation of the particle number can be

calculated exactly as in the classical case (see Chapter 9) from

$$\frac{\sigma_N^2}{N^2} = \frac{kT}{V}\kappa, \qquad \text{with} \qquad \kappa = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_{T,N} \tag{13.73}$$

where κ is the isothermal compressibility. This quantity, however, is infinite, because $\partial p/\partial V|_T = 0$. In other words, the fluctuations around the mean particle number, Equation (13.17), become infinitely large, and a statement concerning the mean particle number is thus only of limited value.

Example 13.2: Planck's radiation formula

We now apply the results of this section to a gas of photons in a cavity resonator with ideally reflecting walls at the temperature T.

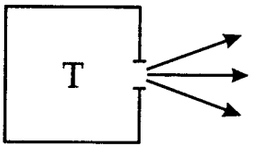


Figure 13.8. Cavity resonator with a photon gas at temperature T.

Especially, we want to calculate the radiative power which leaves the cavity through a small outlet of area dF, as well as the frequency spectrum of the radiation. The special importance of this model system is that the spectral radiation density $Q(\omega, T)$ (radiative power per frequency interval and emitting area) of an arbitrary thermal radiator can be expressed according to *Kirchhoff's law* (see Example 13.4):

$$Q(\omega, T) = A(\omega, T)Q_{\text{black}}(\omega, T)$$

in terms of that of a so-called blackbody. The factor $A(\omega, T)$ is the *absorptivity* of the real body, which depends, as does the spectral density, on the frequency ω of the radiation and the temperature. A blackbody is thus characterized by an absorptivity $A_{\text{black}}(\omega, T) \equiv 1$. One can now readily conclude that the radiation which leaves the cavity resonator through a small hole, is just the radiation of a blackbody. If, on the other hand, a photon of arbitrary frequency hits the hole from the outside, it enters the cavity and is ideally reflected at the walls. The probability of leaving the cavity again through the small hole is negligible small. The hole, therefore, represents an emitter area with absorptivity $A \equiv 1$.

Since there is no body having an absorptivity $A = 1$ in nature, the blackbody is an idealized model system. However, it is very useful, since its spectral radiation density does not depend on any material properties, which solely enter the absorptivity.

The photon gas in the interior of the cavity can now be looked upon as an ultrarelativistic Bose gas, since the photons fulfill the energy–momentum relation

$$\epsilon = c\,|\vec{p}| \qquad \text{with} \qquad \epsilon = \hbar\omega, \quad \vec{p} = \hbar\vec{k} \tag{13.74}$$

if ω denotes the frequency, and $\vec{k}$ denotes the wave number of the photons.

Furthermore, photons have spin one, and therefore behave as bosons. However, we have to take into account a special feature with respect to the additional spin degree of freedom. In principle, a particle with spin s (momentum state $|\vec{p}\rangle$) can possess $2s + 1$ different spin projections which belong to the same energy in the noninteracting case. The one-particle density of states (13.61) should therefore be multiplied by the degeneracy factor $g_s = 2s + 1$. For photons, however, this is not valid, since the electromagnetic field is always transverse and has only two possible polarization degrees of freedom. Thus, for real photons, only the spin projections $s_z = \pm 1$ occur. The projection $s_z = 0$ belonging to longitudinal waves drops

out. The one-particle density of states of the photons thus reads, with the degeneracy factor $g_s = 2$:

$$g(\epsilon) = g_s \frac{4\pi V}{h^3 c^3} \epsilon^2 \qquad g_s = 2 \tag{13.75}$$

The mean occupation number $\langle n_\epsilon \rangle$ of an energy state for photons with the chemical potential $\mu = 0$ is now given by

$$\langle n_\epsilon \rangle = \frac{1}{\exp\{\beta\epsilon\} - 1} \tag{13.76}$$

The number of photons in the energy interval $d\epsilon$ is thus

$$dN(\epsilon) = \langle n_\epsilon \rangle \, g(\epsilon) \, d\epsilon = \frac{8\pi V}{h^3 c^3} \frac{\epsilon^2 \, d\epsilon}{\exp\{\beta\epsilon\} - 1}$$

or, if this is rewritten in terms of the frequency with Equation (13.74), and if $n = N/V$ denotes the spatial density of photons,

$$\frac{dn(\omega)}{d\omega} = \frac{1}{\pi^2 c^3} \frac{\omega^2}{\exp\{\beta\hbar\omega\} - 1} \tag{13.77}$$

Quite analogously, one finds the spatial energy density $u = U/V$ per frequency interval:

$$\frac{du(\omega)}{d\omega} = \hbar\omega \frac{dn(\omega)}{d\omega} = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp\{\beta\hbar\omega\} - 1} \tag{13.78}$$

These quantities, however, refer to the interior of the cavity. With the same considerations as in Exercise 7.6 we can also evaluate the rate R at which photons with frequency ω leave the cavity through the small outlet:

$$R = \frac{d^2 N}{dt \, dF} = \frac{1}{4} \frac{N}{V} \langle v \rangle$$

which gives the number of particles with mean velocity $\langle v \rangle$ which leave a box through a small hole per area and time. In our case, N/V is given by Equation (13.77) (per frequency interval), and the mean velocity of photons is $\langle v \rangle = c$:

$$R(\omega) = \frac{c}{4} \frac{dn(\omega)}{d\omega} = \frac{1}{4\pi^2 c^2} \frac{\omega^2}{\exp\{\beta\hbar\omega\} - 1} \tag{13.79}$$

Each of these photons corresponds to an energy $\hbar\omega$. The energy flux per unit area of the hole and per time and frequency interval is thus

$$\frac{d^3 E}{dF \, d\omega \, dt} = \hbar\omega R(\omega) \tag{13.80}$$

Since the energy per time just yields the radiative power p, Equation (13.80) is, of course, identical with the radiative power per hole area and frequency, i.e., with the spectral density $Q_s(\omega, T)$. We thus have

$$Q_s(\omega, T) = \hbar\omega R(\omega) = \frac{\hbar}{4\pi^2 c^2} \frac{\omega^3}{\exp\{\beta\hbar\omega\} - 1} \tag{13.81}$$

This is the famous *radiation law of Planck* for the spectral radiation density of a blackbody in thermal equilibrium. From a historical point of view, however, Planck obtained this formula in the year 1900 in a slightly different way. It is very instructive to contrast his method with our derivation, which originates from Bose:

Planck did not consider a gas of *indistinguishable photons*, but rather a large number of *distinguishable oscillators*, one for each frequency ω. In this case, one must apply Maxwell-Boltzmann statistics to the oscillators, not Bose-Einstein statistics. However, Planck additionally assumed that the oscillators could absorb or emit only certain energy portions $\hbar\omega$. We have already treated the corresponding problem in the framework of classical Maxwell-Boltzmann statistics in Example 8.1. Accordingly, the mean excitation level of an oscillator with frequency ω is just given by

$$\langle n_\omega \rangle = \frac{1}{\exp\{\beta\hbar\omega\} - 1}$$

which is identical to Equation (13.76). The spectral energy density follows immediately from the mean energy $\langle \epsilon_\omega \rangle$ of an oscillator with frequency ω multiplied by the number of oscillators per frequency interval (state density) and volume as

$$\frac{du(\omega)}{d\omega} = \langle \epsilon_\omega \rangle \frac{g(\omega)}{V} = \left(\frac{\hbar\omega}{\exp\{\beta\hbar\omega\} - 1} + \frac{\hbar\omega}{2} \right) \frac{1}{\pi^2 c^3} \omega^2 \qquad \textbf{(13.82)}$$

where $g(\omega)$ can be obtained from Equation (13.75) by rewriting it in terms of frequencies (note $g(\epsilon) = dN/d\epsilon \rightarrow g(\omega) = dN/d\omega = \hbar g(\epsilon)$).

Expression (13.82) now agrees with Equation (13.78) up to the zero point energy of the oscillators (which was, by the way, not known to Planck). The indistinguishable photons of frequency ω are obviously identical to the single energy portions $\hbar\omega$ of the distinguishable oscillators, and both ways of consideration lead to the same results. However, if the photons were real classical distinguishable ultrarelativistical objects, instead of Equation (13.76) one should have used the expression

$$\langle n \rangle^{\mathrm{MB}} = \exp\{-\beta\epsilon\}$$

The whole derivation also can be performed using this mean occupation number, and one obtains for the spectral radiation density

$$Q_s^{\mathrm{MB}}(\omega, T) = \frac{\hbar}{4\pi^2 c^2} \omega^3 \exp\{-\beta\hbar\omega\}$$

This is *Wien's radiation law*, which was—without knowledge of Planck's constant—already known prior to Planck's radiation law. Here also, the photons are treated as ultrarelativistic particles, but with the difference that they are assumed to be distinguishable. Wien's radiation law is just the classical limit of Equation (13.81) for $\hbar\omega \gg kT$, since then the exponential term in the denominator dominates, compared to unity. In this case, the photons behave nearly like classical particles.

On the other hand, one can also consider the limiting case $kT \gg \hbar\omega$. In this case, the energy portions $\hbar\omega$ are very small compared to the mean thermal excitation energy, and the discrete structure of the energy spectrum of the oscillators no longer plays an important role. One may treat them as classical oscillators. According to the equipartition theorem, each of these oscillators on average has the thermal excitation energy $\langle \epsilon_\omega \rangle = kT$. This corresponds to the purely classical wave picture, according to which each degree of freedom of the radiation field has just the mean energy kT in thermal equilibrium. If one inserts this classical mean energy into Equation (13.82) instead of the mean energy of the quantum mechanical oscillators, it follows that

$$\frac{du(\omega)}{d\omega} = \langle \epsilon_\omega \rangle \frac{g(\omega)}{V} = kT \frac{\omega^2}{\pi^2 c^3}$$

which leads to the *radiation law of Rayleigh and Jeans*:

$$Q_s^{\text{cl.wavepict.}}(\omega, T) = \frac{\omega^2}{4\pi^2 c^2} kT$$

This law also follows from the general formula (13.81) by expanding in the limit $\hbar\omega \ll kT$. Planck's formula thus represents a connection between the classical wave picture (continuous excitation, Rayleigh-Jeans law) and the pure particle interpretation of photons (ultrarelativistic, distinguishable classical particles, Wien's law). It thus contains in a remarkably clear way the wave–particle duality of photons. We want to summarize these perceptions in a little scheme:

Table 13.1 The three radiation laws

Planck's radiation law	$\hbar\omega \gg kT$ Wien's law	$\hbar\omega \ll kT$ Rayleigh–Jeans law
Indistinguishable particles with Bose-Einstein statistics or Distinguishable oscillators with discrete excitation levels	Distinguishable classical particles with Maxwell-Boltzmann statistics	Classical wave picture with mean excitation energy kT per degree of freedom of the radiation field or Classical distinguishable oscillators with continuous excitation energy

The dependence of the three radiation laws on the frequency ω of the radiation is displayed in Figure 13.9 for a certain temperature.

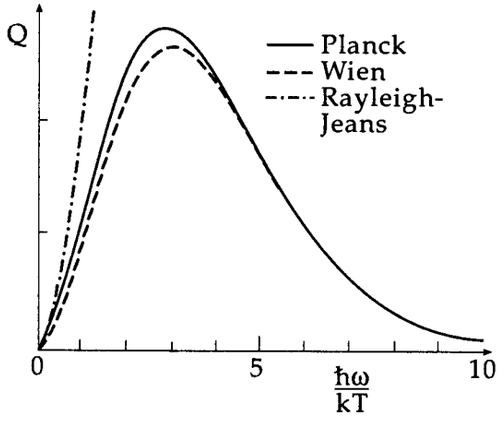


Figure 13.9. The three radiation laws.

The law of Rayleigh and Jeans yields radiation densities at high frequencies that are too high ($Q \to \infty$ for $\omega \to \infty$), since each degree of freedom of the radiation field (each oscillator with frequency ω) has the same mean energy. The number of oscillators per frequency interval, however, increases like ω^2, from which follows this property, commonly known as the *ultraviolet catastrophe*. On the other hand, Wien's law reproduces at least qualitatively the shape of the radiation density. However, it fails just at the middle frequencies. The maximum of Planck's distribution lies at $\hbar\omega_{\max}$, which can be calculated, with $x = \hbar\omega$, from Equation (13.81):

$$\left.\frac{dQ_s(x, T)}{dx}\right|_{x=x_{\max}} = 0 \Rightarrow \exp\{\beta x\}(3 - \beta x) = 3$$

This equation has to be solved numerically, with the result

$$\beta x_{\max} = 2.821 \quad \text{or} \quad \hbar\omega_{\max} = 2.821kT$$

The maximum of the radiation distribution is shifted linearly, proportional to the temperature, to higher frequencies.

For Wien's radiation law it holds quite analogously that $x_{\max} = 3kT$ or $\beta x_{\max} = 3$. The linear shift of the maximum of the distribution with temperature is known as *Wien's shift*

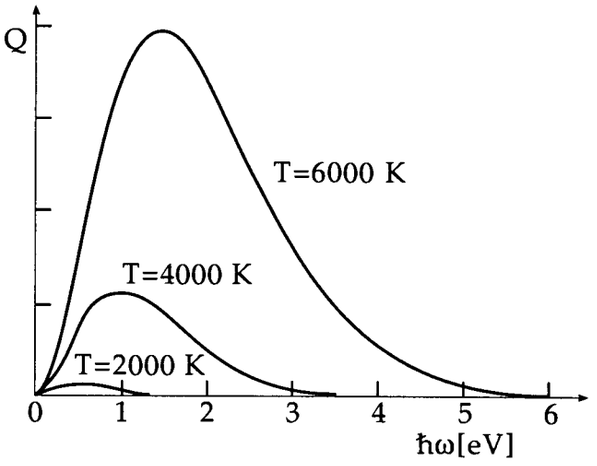


Figure 13.10. Planck's radiation law for different temperatures.

law. In Figure 13.10, Planck's radiation law is shown as a function of frequency for various temperatures. As one observes, at temperatures up to 2000 K only a small fraction of the radiative power falls in the visible range of the spectrum. The largest part of the radiation lies in the infrared region (heat radiation).

This is, for instance, a reason for the small efficiency of light bulbs with respect to the transformation of electrical energy into visible light. The temperature of the filament cannot be larger than the melting point of the material, $T_{\text{melt}}(\text{tungsten}) = 3683$ K. On the other hand, a large part of the radiation of the sun, which has a surface temperature of about 5800 °K lies in the visible range.

Finally, we can calculate the total radiation density $Q(T)$ of a blackbody from

$$Q_{\text{tot}}(T) = \int_0^\infty d\omega Q_s(\omega, T) = \frac{(kT)^4}{4\pi^2\hbar^3c^2} \int_0^\infty dx \frac{x^3}{e^x - 1}$$

where $x = \beta\hbar\omega$ was substituted. The integral has the value $\Gamma(4)g_4(1) = 6\zeta(4) = \pi^4/15$ according to Equation (13.9), and one obtains

$$Q_{\text{tot}}(T) = \sigma T^4 \qquad \text{with} \qquad \sigma = \frac{\pi^2 k^4}{60\hbar^3 c^2} = 5.67 \cdot 10^{-8} \text{ Watt m}^{-2} \text{ K}^{-4}$$

which is known as the *Stefan-Boltzmann law*.

Example 13.3: The cosmic 3K background radiation

As we know, the maximum of Planck's radiation distribution is uniquely related to the temperature, or to the parameter $\beta = 1/kT$ (Wien's shift law). One can therefore draw conclusions about the temperature of a radiating blackbody from its electromagnetic frequency spectrum.

In the year 1964 Penzias and Wilson* discovered an isotropic cosmic radiation, the frequency spectrum of which corresponds to a temperature of nearly 3 K (see Figure 13.11). The experimental efforts to measure this radiation are enormous. At first one has to shield the antenna, which serves as the radiation receiver (at 3 K the maximum of Planck's distribution lies in the radiowave range), against all interference sources, e.g., devices in the vicinity, and

*A. A. Penzias, R. H. Wilson, *Astrophys. Journ.* **142** (1965) 419.

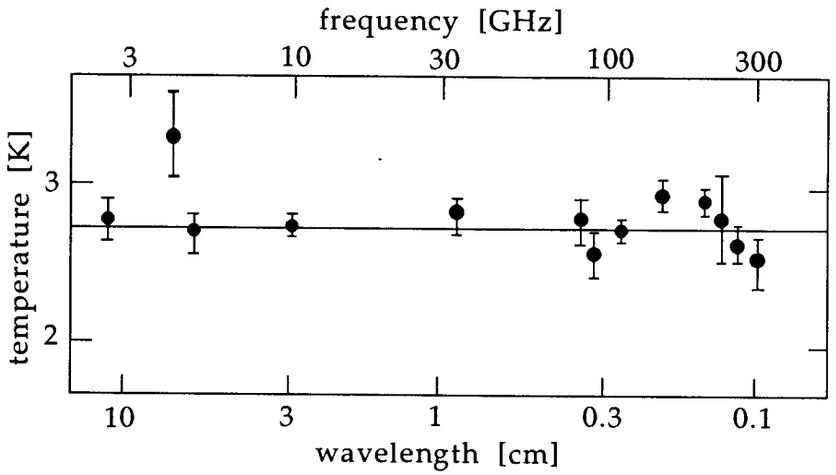


Figure 13.11. Frequency spectrum of the cosmic background radiation.

to cool it below 3 K, to eliminate most of the thermal radiation caused by its own temperature. Further interference factors come from the earth, which radiates with a temperature of 300 K (this cannot be isolated in experiments performed on the ground), as well as interstellar dust clouds, which absorb a part of the frequencies of the background radiation. Therefore, the radiation distribution cannot be measured completely. Another problem in the measurement is the isotropy of the radiation. Since the intensity coming from every direction of the sky is equal, one has no reference point against which to perform a differential comparison of neighboring regions (a method which is commonly used to determine temperatures of cosmic radiation sources). Therefore, one has to use a calibrated radiator for comparison.

The isotropic 3K background radiation plays an important role in many cosmological models. Today we have the following picture of its origin: Shortly after the Big Bang, when the density of matter was still very large, the universe consisted mainly of hydrogen and helium nuclei, as well as free electrons and radiation. The free electrons, which have a large cross section for photons, provided a strong coupling between the radiation and the matter, so that a common temperature of about 4200 K (ionization temperature of H and He) persisted. One can think of the universe as a cavity in which a hot gas of the mentioned constituents was in equilibrium with the cavity radiation.

In its further (adiabatic) expansion the universe steadily cooled down. Below 4200 K the H and He nuclei captured the electrons (recombination), so that the radiation decoupled from the matter because of the essentially reduced cross section for scattering of photons from bound electrons. The gravitation of the expanding matter alone caused a red shift of the radiation, i.e., a decrease of temperature to the actual value of 3 K. Since the mean free path of the photons became very large after the recombination, even today photons exist which were present at the recombination, approximately 10–20 billion years ago. The cosmic background radiation thus contains information about the state of the universe at the time of the recombination.

However, to prove the assertion that the 3K background radiation stems from the recombination of the ionized H and He nuclei, measurements are necessary which exclude other possible radiation sources; e.g., if the recombination theory is correct, the interaction of photons with frequencies in the range of the absorption lines of H and He should have prevailed far longer (due to the large cross section for resonance absorption), so that just at these frequencies deviations from Planck's distribution should be observable. Unfortunately, the already mentioned interference factors prevent precise measurements in this frequency domain, and one may be very eager to await future satellite experiments.

Example 13.4: Derivation of Kirchhoff's law

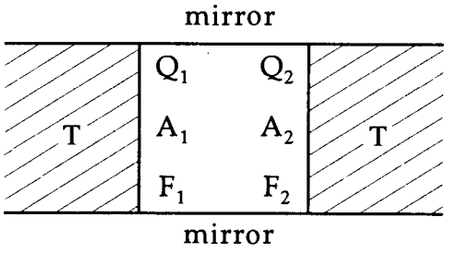


Figure 13.12. Concerning the derivation of Kirchhoff's law.

To derive Kirchoff's law, we consider a model system consisting of two parallel surfaces of equal size and temperature T, which are isolated from the surroundings by ideally reflecting mirrors, so that no radiation can escape from between them (see Figure 13.12). The two surfaces may possess absorptivities A_1 and A_2, respectively, and spectral radiation densities Q_1 and Q_2.

The whole setup may be enclosed by adiabatic walls, so that there is also no heat exchange with the surroundings. Area a_1 emits the radiative power Q_1 to area a_2, a part A_2Q_1 of which is absorbed and a part $(1 - A_2)Q_1$ of which is reflected. Vice versa, area a_2 emits the radiative power Q_2 onto area a_1, a part A_1Q_2 of which is absorbed and a part $(1 - A_1)Q_2$ of which is reflected. In thermodynamic equilibrium, however, the effective energy flux between both surfaces has to vanish. For instance, if the flux from a_1 to a_2 were to dominate, the surface a_2 would be heated up in comparison to a_1, which contradicts the second law of thermodynamics. The total energy flux from a_1 is given by the direct part Q_1 and the reflected part $(1 - A_1)Q_2$. Analogously, the energy flux from a_2 is the sum of Q_2 and $(1 - A_2)Q_1$. In thermodynamic equilibrium it thus holds that

$$Q_1 + (1 - A_1)Q_2 = Q_2 + (1 - A_2)Q_1 \Leftrightarrow \frac{Q_1}{Q_2} = \frac{A_1}{A_2}$$

The radiation densities of the two plates must therefore behave exactly as the two absorptivities. If now, for example, plate a_1 is completely black ($A_1 = 1$ and $Q_1 = Q_{\text{black}}$), the spectral radiation density of plate a_2 is

$$Q_2 = A_2 Q_{\text{black}}$$

which corresponds exactly to *Kirchhoff's law*.

Example 13.5: Lattice oscillations in a solid: Einstein and Debye model

The interaction potential between two atoms in a crystalline solid has approximately the shape depicted in Figure 13.13. The equilibrium position is characterized by the distance d. Of course, this is only a crude approximation of the true situation in a solid, where the potential energy of a particle may also depend on the spatial direction of the elongation. The essential property of a stable equilibrium position at a distance d, which is of the order of the lattice constant, is, however, correctly reproduced by this potential.

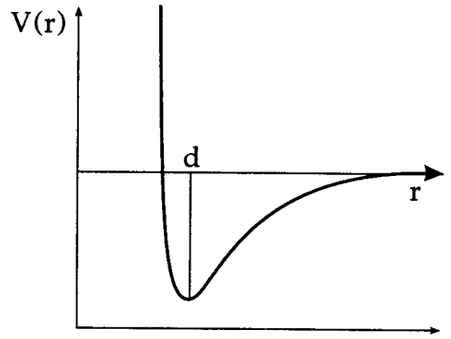


Figure 13.13. Interaction potential of two atoms in a solid (schematical).

If one restricts oneself to small shifts of the atoms from their rest position, one may even expand the potential around the equilibrium position and truncate the expansion after the quadratic term,

$$V(x_1, \ldots, x_N) = V(\overline{x_1}, \ldots, \overline{x_N}) + \sum_i \left.\frac{\partial V}{\partial x_i}\right|_{\overline{x_1},\ldots,\overline{x_N}} (x_i - \overline{x_i}) + \frac{1}{2} \sum_{i,k} \left.\frac{\partial^2 V}{\partial x_i \partial x_k}\right|_{\overline{x_1},\ldots,\overline{x_N}} (x_i - \overline{x_i})(x_k - \overline{x_k}) + \cdots$$

However, if the $\overline{x_1}, \ldots, \overline{x_N}$ are the equilibrium positions of the particles, the coefficients $\partial V/\partial x_i$ of the linear term have to vanish. If one denotes the coefficients of the quadratic term by α_{ik} and considers only the relative shift with respect to the rest position $\xi_i = x_i - \overline{x_i}$, one obtains, after neglecting the constant term,

$$V(\xi_i) = \sum_{i,k=1}^{N} \alpha_{ik} \xi_i \xi_k$$

The corresponding Hamiltonian is

$$H(\xi_i) = \sum_{i=1}^{N} \frac{1}{2} m \dot{\xi}_i^2 + \sum_{i,k=1}^{N} \alpha_{ik} \xi_i \xi_k$$

From classical mechanics one knows that there exists a canonical transformation of the ξ_i to new generalized coordinates q_i, so that H attains, in terms of the new coordinates, the form

$$H(q_i) = \sum_{i=1}^{3N} \frac{1}{2} m_i \left(\dot{q}_i^2 + \omega_i^2 q_i^2\right)$$

The new coordinates correspond to the normal oscillations of the solid with the eigenfrequencies ω_i and the effective masses m_i.

Here we do not want to discuss the corresponding classical problem in detail. For our purpose it is sufficient to know that the Hamiltonian has the form of that of $3N$ harmonic oscillators with different frequencies ω_i. The eigenfrequencies ω_i and effective masses follow from the matrix α_{ik} and from the particle masses m. (For a solid of finite size, 6 of the degrees of freedom of the "normal oscillations" actually describe translations and rotations of the whole solid, but we want to assume $N \gg 1$.) Furthermore, we do not even want to calculate the eigenfrequencies ω_i in detail for a certain solid with a definite lattice structure, but instead we want to make assumptions concerning the frequency spectrum that are as simple and clear as possible.

The most simple possibility was proposed by Einstein. He assumed that all $3N$ eigenfrequencies of the normal oscillations are identical and have a fixed value ω. Then our model of a solid corresponds to an ensemble of $3N$ distinguishable oscillators with frequency ω, which, however, we have to treat quantum mechanically (discrete excitation levels). The corresponding statistical problem was already discussed in Example 8.1 using Maxwell-Boltzmann statistics, and we can immediately write down the thermodynamic properties of our model

system. For instance, the internal energy is

$$U(N, V, T) = 3N\hbar\omega \left(\frac{1}{2} + \frac{1}{\exp\{\beta\hbar\omega\} - 1} \right) \tag{13.83}$$

Here

$$\langle n \rangle = \frac{1}{\exp\{\beta\hbar\omega\} - 1} \tag{13.84}$$

is again the average excitation level of an oscillator with frequency ω at temperature T. The average energy of such an oscillator is then $\langle \epsilon \rangle = \hbar\omega \left(\frac{1}{2} + \langle n \rangle \right)$, from which Equation (13.83) follows immediately. However, we can interpret Equation (13.83) also in somewhat different terms, if we do not conceive $\langle n \rangle$ as the average excitation level of an oscillator, but as the number of indistinguishable excitation quanta per oscillator, so–called *phonons*, which have the absolute value $\hbar\omega$. Just as photons are the energy quanta of the electromagnetic field, phonons are the energy quanta of the normal oscillations of a solid. Like photons, phonons are obviously bosons with an energy–momentum relationship

$$\epsilon = c_s |\vec{p}|, \qquad \text{with} \qquad \epsilon = \hbar\omega, \quad \vec{p} = \hbar\vec{k}$$

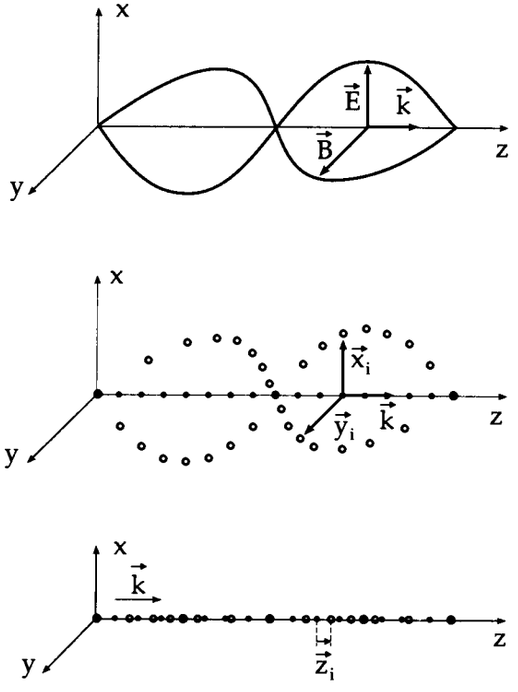


Figure 13.14. Concerning the analogy between electromagnetic waves and sound waves in the solid.

if ω denotes the frequency of the normal oscillations and $\vec{k}$ the wave numbers. However, c_s is *not* the velocity of light, as in the case of photons, but the propagation velocity of oscillations in the solid, i.e., *the velocity of sound.* The number of phonons in the solid is as well undetermined as the number of photons in the radiation field; thus the chemical potential vanishes. However, while in the electromagnetic case there exists just one oscillator for each frequency and their total number is infinite (even continuously infinite, if the field is not confined in a box with ideally conducting walls), we have in the case of the sound field in the solid only one frequency and $3N$ oscillators, provided we consider the Einstein model.

The analogy between electromagnetic waves and sound waves in the solid can be followed further.* The electromagnetic field is described by the amplitudes of the $\vec{E}$ or $\vec{B}$ field. These are always perpendicular to the propagation direction $\vec{k}$, which we choose to be the z-axis. The position of the field vector in the xy-plane corresponds to the two degrees of freedom of the polarization (spin projection).

Quite analogously, the sound field is described by the displacements of the single atoms. Apart from the two possibilities for transverse waves with displacements in x- or y-directions perpendicular to the propagation direction $\vec{k}$, there are now, however, also longitudinal waves, with displacements in direction of $\vec{k}$. In general, the propagation velocity (velocity of sound) for *longitudinal and transverse waves*, c_{sl} or c_{st}, respectively, is different. Obviously, phonons, like photons, have spin 1. The two

*(Figure 13.14.)

spin projections $s_z = \pm 1$ correspond to the two transverse modes, and $s_z = 0$ corresponds to the longitudinal mode, which does not exist in the electromagnetic case.

An especially interesting thermodynamic property is the specific heat of solids, which shall now be calculated within the Einstein model:

$$C_V = \left.\frac{\partial U}{\partial T}\right|_{V,N} = 3Nk(\beta\hbar\omega)^2 \frac{\exp\{\beta\hbar\omega\}}{(\exp\{\beta\hbar\omega\} - 1)^2} \tag{13.85}$$

The function

$$E(x) = \frac{x^2 e^x}{(e^x - 1)^2}$$

is called the *Einstein function.*

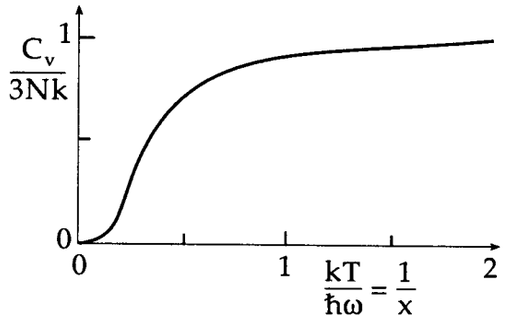


Figure 13.15. Specific heat of solids according to Equation (13.85).

Indeed, Equation (13.85) yields qualitatively the correct functional dependence of the specific heat of solids (Figure 13.15). For large temperatures, the rule of Dulong and Petit is obtained; i.e., $C_V = 3Nk$ in the classical limit ($kT \gg \hbar\omega$); for small temperatures, the specific heat converges to zero as $C_V \propto x^2 e^{-x}$ in the Einstein model. However, precise measurements have shown that C_V does not drop exponentially towards zero, but only as T^3.

Obviously the assumption of only one oscillation frequency is too inaccurate to obtain quantitative agreement with experiment. We now want to improve the simple Einstein model by permitting a whole frequency spectrum. In the thermodynamic limit ($V \to \infty, N \to \infty, N/V = \text{const.}$) the frequencies of the normal oscillations are arbitrarily close to each other, and we can calculate their number per frequency interval in the same way as in the case of photons. Also the phonons behave like "ultrarelativistic" free particles. The density of states is according to Equation (13.61):

$$g(\epsilon) = \frac{\partial \Sigma}{\partial \epsilon} = \frac{4\pi V}{h^3 c^3}\epsilon^2$$

or

$$g(\omega) = \frac{\partial \Sigma}{\partial \omega} = \frac{V}{2\pi^2 c^3}\omega^2$$

The total number of oscillators (normal oscillations) per frequency interval follows from the two transverse modes and the one longitudinal mode as

$$g(\omega) = V\left(\frac{\omega^2}{2\pi^2 c_t^3} + \frac{\omega^2}{\pi^2 c_t^3}\right) \tag{13.86}$$

However, the number of all normal oscillations in the solid is finite ($3N$) and not infinite as in the case of the electromagnetic field. The reason is that the solid is not a continuous medium, but possesses a discrete structure with a lattice constant d. Thus, no waves can propagate inside the solid which have a wavelength that is smaller than the lattice constant. The density of states $g(\omega)$ must therefore be truncated at a minimum wavelength, or because $\lambda \propto \omega^{-1}$, at a maximum frequency ω_c, the so–called *"cut–off" frequency.* We determine ω_c from the

requirement

$$\int_0^{\omega_c} g(\omega)\,d\omega = 3N \qquad \text{or} \qquad \omega_c^3 = 18\pi^2 \frac{N}{V}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)^{-1} \tag{13.87}$$

The model of lattice oscillations corresponding to Equations (13.86) and (13.87) originates from Debye. The energy density in the frequency interval $d\omega$ now follows exactly as in Example 13.2

$$\frac{du(\omega)}{d\omega} = \langle\epsilon\rangle \frac{g(\omega)}{V} = \left(\frac{1}{\exp\{\beta\hbar\omega\} - 1} + \frac{1}{2}\right)\hbar\omega 9 \frac{N}{V}\frac{\omega^2}{\omega_c^3}, \qquad \omega \le \omega_c \tag{13.88}$$

where the density of states $g(\omega)$ was expressed in terms of ω_c,

$$g(\omega) = \begin{cases} 9N\dfrac{\omega^2}{\omega_c^3} & \omega \le \omega_c \\ 0 & \omega > \omega_c \end{cases}$$

The internal energy follows by integrating Equation (13.88) up to the cut-off and multiplying the result by V:

$$U(T, V, N) = \frac{9N\hbar}{\omega_c^3}\int_0^{\omega_c} d\omega \left(\frac{1}{\exp\{\beta\hbar\omega\} - 1} + \frac{1}{2}\right)\omega^3$$

From this one obtains for the specific heat

$$C_V = \left.\frac{\partial U}{\partial T}\right|_{V,N} = \frac{9N\hbar^2}{\omega_c^3 kT^2}\int_0^{\omega_c} d\omega \frac{\omega^4 \exp\{\beta\hbar\omega\}}{(\exp\{\beta\hbar\omega\} - 1)^2}$$

or, after substituting $x = \beta\hbar\omega$,

$$C_V = 9Nk\left(\frac{kT}{\hbar\omega_c}\right)^3 \int_0^{x_0} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

In analogy to the Einstein function one calls

$$\mathcal{D}(x_0) = \frac{3}{x_0^3}\int_0^{x_0} dx \frac{x^4 e^x}{(e^x - 1)^2} \qquad \text{with} \qquad x_0 = \frac{\hbar\omega_c}{kT} \tag{13.89}$$

the *Debye function*, and it holds that $C_V = 3Nk\mathcal{D}(x_0)$. In the Einstein model, the thermodynamic quantities depend on the frequency of the oscillators. In the Debye model, this role is assumed by the cut-off frequency ω_c. The parameter combination $\Theta = \hbar\omega_c/k$ has the dimension of a temperature. It is known as *Debye temperature*. In principle, this temperature (or ω_c, respectively,) can be calculated from the measured sound velocities, but this procedure is not very accurate. Thus, one does better to fit the parameter Θ (or ω_c) directly to the shape of the specific heats.

Before comparing the theory with experiment, we investigate the limiting cases $x_0 \ll 1$ (classical limit) and $x_0 \gg 1$. For $x_0 \to 0$, we obtain after an integration by parts of the term $e^x/(e^x - 1)^2$ in Equation (13.89),

$$\begin{aligned} \mathcal{D}(x_0) &= \frac{3}{x_0^3}\left\{-\left.\frac{x^4}{e^x - 1}\right|_0^{x_0} + \int_0^{x_0} dx \frac{4x^3}{e^x - 1}\right\} \\ &= -\frac{3x_0}{e^{x_0} - 1} + \frac{12}{x_0^3}\int_0^{x_0} \frac{x^3}{e^x - 1}\,dx \end{aligned} \tag{13.90}$$

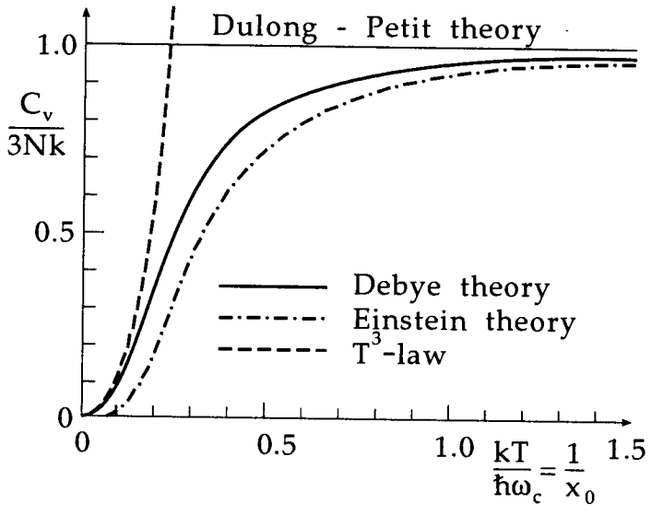


Figure 13.16. Frequency distribution of the lattice oscillations.

If one now expands $(e^x - 1)^{-1}$ for small x, one has

$$\frac{1}{e^x - 1} = \frac{1}{x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \cdots} = \frac{1}{x}\frac{1}{1 + \frac{1}{2}x + \frac{1}{6}x^2 + \cdots}$$

The last term can be expanded for $x \ll 1$ according to the formula

$$\frac{1}{f(x)} = 1 - a_1 x - (a_2 - a_1^2)x^2 - \cdots \qquad \text{for} \qquad f(x) = 1 + a_1 x + a_2 x^2 + \cdots$$

thus,

$$\frac{1}{e^x - 1} = \frac{1}{x}\left(1 - \frac{1}{2}x + \frac{1}{12}x^2 + \cdots\right)$$

If one inserts this into Equation (13.90), it follows with $x_0 \ll 1$ that

$$\begin{aligned}
\mathcal{D}(x_0) &\approx -3\left(1 - \frac{1}{2}x_0 + \frac{1}{12}x_0^2 + \cdots\right) \\
&\quad + \frac{12}{x_0^3}\int_0^{x_0} x^2\left(1 - \frac{1}{2}x + \frac{1}{12}x^2 + \cdots\right)dx \\
&\approx -3 + \frac{3}{2}x_0 - \frac{1}{4}x_0^2 + \cdots + 4 - \frac{3}{2}x_0 + \frac{1}{5}x_0^2 + \cdots \\
&\approx 1 - \frac{x_0^2}{20} + \cdots
\end{aligned}$$

The specific heat thus becomes constant in the classical limit $x_0 \to 0$, $C_V = 3Nk$, as we expected, and decreases for lower temperatures. In the limit $x_0 \to \infty$ we find from Equation (13.90):

$$\begin{aligned}
\mathcal{D}(x_0) &\approx -3x_0 \exp\{-x_0\} + \frac{12}{x_0^3}\int_0^{\infty} \frac{x^3}{e^x - 1}dx \\
&\approx \frac{12}{x_0^3} 6g_4(1) = \frac{4}{5}\frac{\pi^4}{x_0^3} = \frac{4}{5}\pi^4\left(\frac{kT}{\hbar\omega_c}\right)^3
\end{aligned}$$

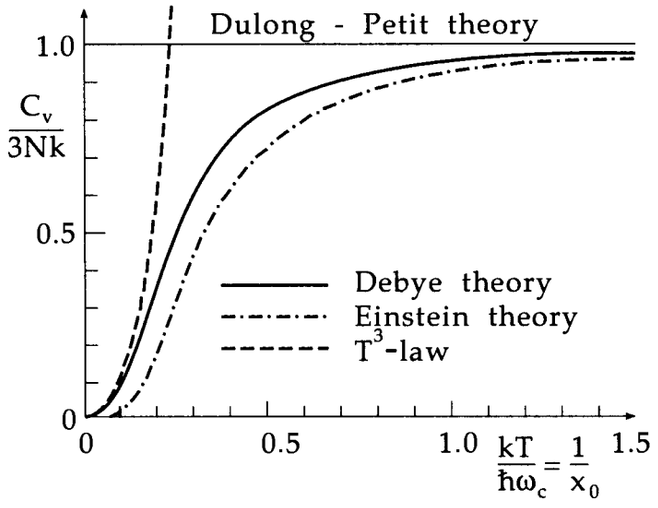


Figure 13.16. Specific heat of solids.

since the term proportional to $\exp\{-x_0\}$ decreases exponentially, and the integral has the value $\Gamma(4)g_4(1)$ according to Equation (13.9). Hence, we find indeed that the specific heat increases like T^3 for small temperatures.

In Figure 13.14, the specific heat of the Debye model (solid line) is shown in comparison to the specific heat of the Einstein model (dashed-dotted line), as well as the T^3 law for low temperatures.

In Table 13.2, some Debye temperatures for different materials are shown. For comparison, not only values obtained by a best fit of the theoretical specific heats to the data are shown, but also values determined via the elastic constants of the solid (velocities of sound).

Especially interesting is the extremely high Debye temperature of diamond. The corresponding high cut–off frequency can be interpreted by the fact that a diamond is a very incompressible (rigid) crystal, the lattice oscillations of which have high excitation energies. The specific heat of diamond does not obey the rule of Dulong and Petit at room temperature, but is still temperature dependent and much smaller than that of metals.

One can also directly compare the frequency distribution $g(\omega)$ of the Debye model with the experimental data shown in Figure 13.16, which were obtained by X–ray scattering (Walker 1956).* As one observes, the Debye model reproduces the experimental shape of the frequency spectrum only very schematically. It is astonishing that this crude model describes the specific heats of solids so well.

TABLE 13.2 Debye temperatures

Crystal	Pb	Ag	Zn	Cu	Al	C	NaCl	KCl	MgO
$\Theta^{\text{spec.h.}}$[K]	88	215	308	345	398	1850	308	233	850
Θ^{elast}[K]	73	214	305	332	402	–	320	240	950

*C. B. Walker, *Phys. Rev* **103** (1956) 547.

14 Ideal Fermi Gas

A further, very useful model system is that of a noninteracting non relativistic gas of Fermi particles. Nucleons in atoms, as well as electrons in metals, can be regarded as an ideal Fermi gas to first approximation. The case $T \to 0$ has here a special importance. The thermodynamic properties of the ideal Fermi gas follow immediately from the logarithm of the grand partition function (cf. Equation (12.37))

$$q(T, V, z) = \ln \mathcal{Z} = \sum_k \ln(1 + z \exp\{-\beta\epsilon_k\}) \tag{14.1}$$

where the sum runs over all one-particle energy eigenstates. The fugacity $z = \exp\{\mu/kT\}$ is to be determined for a given particle number from

$$N(T, V, z) = \sum_k \langle n_k \rangle = \sum_k \frac{1}{z^{-1} \exp\{\beta\epsilon_k\} + 1} \tag{14.2}$$

Here, all values of μ may occur, so that $0 \leq z \leq \infty$. Since it is the mean energy necessary to add another particle to the system, μ must increase with the particle number at fixed volume. The reason is that the Pauli principle requires an energetically higher state for each new particle. We want to rewrite the sums in Equations (14.1) and (14.2) in terms of integrals, as at the beginning of Chapter 13, since the energy eigenstates are arbitrarily close to each other in a large volume:

$$q(T, V, z) = \int_0^\infty d\epsilon\, g(\epsilon) \ln(1 + z \exp\{-\beta\epsilon\}) \tag{14.3}$$

$$N(T, V, z) = \int_0^\infty d\epsilon\, g(\epsilon) \frac{1}{z^{-1} \exp\{\beta\epsilon\} + 1} \tag{14.4}$$

In principle, we may take the one-particle state density $g(\epsilon)$ directly from Equation (13.6). However, since the particles possess $2s + 1$ different spin orientations which are energetically degenerate in the interaction free case, Equation (13.6) must be multiplied by an additional degeneracy factor $g = 2s + 1$:

$$g(\epsilon) = g \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} \tag{14.5}$$

If one inserts this and integrates the term $\epsilon^{1/2}$ in Equation (14.3) by parts, it follows that

$$q(T, V, z) = g\frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty d\epsilon\epsilon^{1/2}\ln(1 + z\exp\{-\beta\epsilon\})$$

$$= g\frac{2\pi V}{h^3}(2m)^{3/2}\frac{2}{3}\beta\int_0^\infty d\epsilon\frac{\epsilon^{3/2}}{z^{-1}\exp\{\beta\epsilon\} + 1} \tag{14.6}$$

$$N(T, V, z) = g\frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty d\epsilon\frac{\epsilon^{1/2}}{z^{-1}\exp\{\beta\epsilon\} + 1} \tag{14.7}$$

Quite analogously to the ideal Bose gas, these integrals may be expressed by standard functions with the help of the substitution $x = \beta\epsilon$. We define

$$f_n(z) = \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}\,dx}{z^{-1}e^x + 1}, \qquad 0 \le z \le \infty \tag{14.8}$$

with the Gamma function defined in Example 1.2, and obtain for Equations (14.6) and (14.7)

$$q(T, V, z) = \frac{pV}{kT} = \frac{gV}{\lambda^3}f_{5/2}(z) \tag{14.9}$$

$$N(T, V, z) = \frac{gV}{\lambda^3}f_{3/2}(z) \tag{14.10}$$

Again, we first investigate the properties of the functions $f_n(z)$. For $z < 1$ we may denote a series expansion:

$$\frac{1}{z^{-1}e^x + 1} = ze^{-x}\frac{1}{1 + ze^{-x}} = ze^{-x}\sum_{k=0}^{\infty}(-ze^{-x})^k = \sum_{k=1}^{\infty}(-1)^{k-1}z^k e^{-kx} \tag{14.11}$$

If one inserts this into Equation (14.8), one obtains

$$f_n(z) = \frac{1}{\Gamma(n)}\sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^n}\int_0^\infty dy y^{n-1}e^{-y} = \sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^n} \tag{14.12}$$

where $y = kx$, and the definition of the Γ–function was used in the calculation of the integral. The only, but essential, difference to the functions $g_n(z)$ in the Bose case (see Equation (13.14)) is the alternating sign of the series (14.12). For the derivative of $f_n(z)$ with respect to the argument, the recursion formula

$$\frac{\partial}{\partial z}f_n(z) = \frac{1}{z}f_{n-1}(z) \tag{14.13}$$

holds, which is immediately clear from the series expansion (14.12). Equation (14.13) holds not only for $z < 1$, but also in general, as one readily convinces oneself:

$$z\frac{\partial}{\partial z}f_n(z) = \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}z^{-1}e^x}{(z^{-1}e^x + 1)^2}\,dx$$

$$= \frac{1}{\Gamma(n)}\left[-\frac{x^{n-1}}{z^{-1}e^x + 1}\Bigg|_0^\infty + (n-1)\int_0^\infty \frac{x^{n-2}}{z^{-1}e^x + 1}\,dx\right] \tag{14.14}$$

The first term in the square brackets vanishes for $n > 1$. Because $\Gamma(n) = (n-1)\Gamma(n-1)$, Equation (14.13) follows.

For large values of z it is useful to set $z = e^y$, with $y = \beta\mu$, and to consider $y \to \infty$. The term $(e^{x-y} + 1)^{-1}$ is then the essential factor in the integrand of Equation (14.8). For $x < y$ and $y \to \infty$, it has the value 1 and for $x > y$ and $y \to \infty$, the value 0. Thus, in this case we obtain a step function, as we have already noticed in the discussion of the occupation numbers in the limit $T \to 0 (y \to \infty)$. For large y it is therefore practical to expand in terms of small deviations from the step function. As an abbreviation, we set $F_n(y) = \Gamma(n) f_n(z)$, with $z = e^y$, and obtain

$$\begin{aligned} F_n(y) &= \int_0^\infty \frac{x^{n-1}\,dx}{e^{x-y}+1} \\ &= \int_0^\infty dx\, x^{n-1}\left[\Theta(y-x) + \left(\frac{1}{e^{x-y}+1} - \Theta(y-x)\right)\right] \\ &= \frac{y^n}{n} + \int_0^\infty dx\, x^{n-1}\left(\frac{1}{e^{x-y}+1} - \Theta(y-x)\right) \end{aligned} \tag{14.15}$$

where the integral is now a small quantity. We perform this integral as follows:

$$\begin{aligned} I &= \int_0^\infty dx\, x^{n-1}\left(\frac{1}{e^{x-y}+1} - \Theta(y-x)\right) \\ &= \int_0^y dx\, x^{n-1}\left(\frac{1}{e^{x-y}+1} - 1\right) + \int_y^\infty x^{n-1}\,dx\,\frac{1}{e^{x-y}+1} \\ &= -\int_0^y dx\,\frac{x^{n-1}}{1+e^{y-x}} + \int_y^\infty dx\,\frac{x^{n-1}}{e^{x-y}+1} \end{aligned} \tag{14.16}$$

In the first integral we now substitute $y - x = u$, and in the second $x - y = v$:

$$I = \int_y^0 du\,\frac{(y-u)^{n-1}}{1+e^u} + \int_0^\infty dv\,\frac{(y+v)^{n-1}}{1+e^v} \tag{14.17}$$

Because $y \gg 1$ we may also take $y \to \infty$ as the integration bound of the first integral. Afterwards we can write the two integrals as one if we set $u = v$:

$$I \approx \int_0^\infty du\,\frac{(y+u)^{n-1} - (y-u)^{n-1}}{1+e^u} \tag{14.18}$$

The two power functions in the numerator are then expanded according to the binomial expansion (for arbitrary real $(n-1)$) in terms of u/y $(y \gg 1)$. All of the even terms drop out:

$$F_n(y) = \frac{y^n}{n} + 2\sum_{j=0}^{\infty}\binom{n-1}{2j+1} y^{n-1-(2j+1)} \int_0^\infty \frac{u^{2j+1}}{e^u+1}\,du \tag{14.19}$$

The integrals can be evaluated with the help of Riemann's ζ–function. Because $e^{-u} < 1$ in the whole range of integration and because

$$\frac{1}{e^u + 1} = \frac{e^{-u}}{1 + e^{-u}} = e^{-u} \sum_{k=0}^{\infty} (-1)^k \exp\{-ku\} \tag{14.20}$$

it holds that

$$\begin{aligned}
\int_0^\infty \frac{u^{2j+1}}{e^u + 1}\, du &= \int_0^\infty du u^{2j+1} e^{-u} \sum_{k=0}^{\infty} (-1)^k \exp\{-ku\} \\
&= \int_0^\infty du u^{2j+1} \sum_{k=1}^{\infty} (-1)^{k-1} \exp\{-ku\} \\
&= \sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{k^{2j+2}} \int_0^\infty dw w^{2j+1} e^{-w} \\
&= \Gamma(2j+2) \sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{k^{2j+2}} \qquad \textbf{(1 4.21)}
\end{aligned}$$

Here we have substituted $w = ku$ in the last step and calculated the integral with the help of the Γ–function. The sum in Equation (14.21) would be exactly equal to the ζ–function, if the even terms did not have the wrong sign. We simply add the even terms and subtract them again twice:

$$\begin{aligned}
\sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{k^l} &= \sum_{k=1}^{\infty} \frac{1}{k^l} - 2 \sum_{k=1}^{\infty} \frac{1}{(2k)^l} \\
&= \sum_{k=1}^{\infty} \frac{1}{k^l} \left(1 - \frac{2}{2^l}\right) \\
&= \zeta(l) \left(1 - \frac{1}{2^{l-1}}\right) \qquad \textbf{(14.22)}
\end{aligned}$$

We therefore have the series expansion

$$F_n(y) = \frac{y^n}{n} + 2 \sum_{j=0}^{\infty} \binom{n-1}{2j+1} y^{n-(2j+2)} \Gamma(2j+2) \zeta(2j+2) \left(1 - \frac{1}{2^{2j+1}}\right) \tag{14.23}$$

and finally

$$f_n(y) = \frac{y^n}{\Gamma(n+1)} \left[1 + \sum_{j=1}^{\infty} 2 \binom{n-1}{2j-1} n y^{-2j} \Gamma(2j) \zeta(2j) \left(1 - \frac{1}{2^{2j-1}}\right)\right] \tag{14.24}$$

As one observes, y^n is the dominant term, and the sum in the brackets represents only a small correction for $y \gg 1$. This formula was first given by Sommerfeld in 1928. Note that the ζ–function with even argument is analytically known.

We want to add a remark. In the second step of the formula (14.16) we have made the approximation $y \to \infty$ at the integration limit. Thus, Equation (14.24) is not a rigorous expansion of the $f_n(z)$ in a mathematical sense. However, the neglected terms are exponentially small: a detailed analysis* shows that only a term $\cos\{(n-1)\pi\}\, f_n(-y)$ is missing in Equation (14.24). Because $f_n(-y) = f_n(1/z)$, this term is exponentially small for $y \gg 1$. For $n = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ the expansion (14.24) is always correct, since then the second term proportional to $\cos\{(n-1)\pi\}$ vanishes.

We now have a good idea how the $f_n(z)$ look (Figure 14.1). Because of Equation (14.13) it holds that

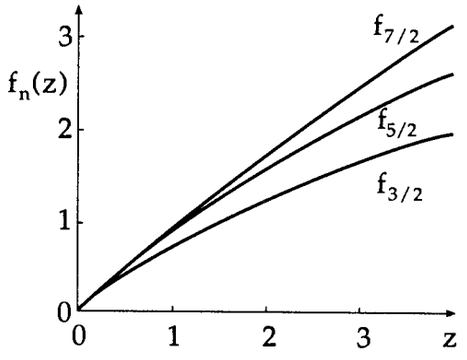


Figure 14.1. The functions $f_n(z)$.

$$f_n(z) \approx z, \qquad z \ll 1 \tag{14.25}$$

and because of Equation (14.24),

$$f_n(z) \approx \frac{(\ln z)^n}{n!}, \qquad z \gg 1 \tag{14.26}$$

For $z = 1$, values can be given; with Equations (14.12) and (14.22) we obtain

$$f_n(1) = \left(1 - \frac{1}{2^{n-1}}\right)\zeta(n) \tag{14.27}$$

e.g., $f_{3/2}(1) = 0.765$, $f_{5/2}(1) = 0.866$, and $f_{7/2}(1) = 0.9277$. Since $f_n(z) > 0$ and $\frac{\partial}{\partial z} f_n(z) = \frac{1}{z} f_{n-1}(z) > 0$, the $f_n(z)$ are strictly monotonous functions and uniquely invertible.

We now return to the thermodynamics of the Fermi gas. First we calculate the internal energy of the system via

$$U = -\frac{\partial}{\partial\beta} \ln \mathcal{Z}\bigg|_{z,V} = kT^2 \frac{\partial}{\partial T} \ln \mathcal{Z}\bigg|_{z,V} = \frac{3}{2} kT \frac{gV}{\lambda^3} f_{5/2}(z) \tag{14.28}$$

With Equation (14.10) the term gV/λ^3 can be eliminated, with the result

$$U = \frac{3}{2} NkT \frac{f_{5/2}(z)}{f_{3/2}(z)} \tag{14.29}$$

which is completely analogous to Equation (13.48), for the Bose gas. In particular, the classical limit follows for $N\lambda^3/(gV) \ll 1$ (small densities, high temperatures). From Equation (14.10) then follows immediately $z \ll 1$, and because of Equation (14.25), $U = \frac{3}{2} NkT$. A comparison of Equations (14.28) and (14.9) yields

$$p = \frac{2}{3} \frac{U}{V} \tag{14.30}$$

*P. Rhodes, *Proc. Roy. Soc. London* **A 204** (1950) 396; R. B. Dingle, *J. App. Res.* **B6** (1956) 225.

Exactly as for the classical ideal Maxwell-Boltzmann gas and for the ideal Bose gas, the pressure is just 2/3 times the energy density. Thus, this formula holds in general for nonrelativistic ideal gases.

The specific heat can be obtained by differentiating the internal energy with respect to the temperature. To this end, however, we need (employing the chain rule) the derivative of z with respect to T. We do this exactly as in Equation (13.52). With Equation (14.10) we find

$$\frac{\partial}{\partial T} f_{3/2}(z) = \frac{\partial}{\partial T}\left(\frac{N\lambda^3}{Vg}\right)$$

$$\frac{\partial z}{\partial T}\frac{1}{z} f_{1/2}(z) = -\frac{3}{2T}\left(\frac{N\lambda^3}{Vg}\right) = -\frac{3}{2T} f_{3/2}(z) \tag{14.31}$$

or

$$\left.\frac{\partial z}{\partial T}\right|_{V,N} = -\frac{3}{2}\frac{z}{T}\frac{f_{3/2}(z)}{f_{1/2}(z)} \tag{14.32}$$

Thus, using Equation (14.13) the specific heat becomes

$$C_V = \frac{\partial U}{\partial T} = \frac{3}{2} Nk \frac{f_{5/2}(z)}{f_{3/2}(z)} + \frac{3}{2} NkT\left[1 - \frac{f_{5/2}(z) f_{1/2}(z)}{(f_{3/2}(z))^2}\right]\left(-\frac{3}{2T}\frac{f_{3/2}(z)}{f_{1/2}(z)}\right)$$

$$\frac{C_V}{Nk} = \frac{15}{4}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4}\frac{f_{3/2}(z)}{f_{1/2}(z)} \tag{14.33}$$

which is again quite analogous to the Bose gas (Equation (13.53). For $z \to 0$, Equation (14.33) just yields the classical value $C_V = \frac{3}{2}Nk$. The free energy $F = U - TS = N\mu - pV$ is easily calculated, using $\mu = kT \ln z$ and p from Equations (14.9) and (14.10):

$$F = N\mu - pV = NkT\left\{\ln z - \frac{f_{5/2}(z)}{f_{3/2}(z)}\right\} \tag{14.34}$$

For the entropy one obtains

$$S = \frac{1}{T}(U - F) = Nk\left\{\frac{5}{2}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \ln z\right\} \tag{14.35}$$

A comparison with the results of Example 9.1 shows that these formulas also reproduce the classical case for $z \ll 1$. As for the Bose gas, the classical limit holds if

$$f_{3/2}(z) = \frac{N}{gV}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} \ll 1 \Rightarrow f_{3/2}(z) \approx z, \qquad z \ll 1 \tag{14.36}$$

If the expression $N\lambda^3/(gV)$ is small, but not very small, one can successively eliminate the fugacity from the series expansion of the $f_n(z)$ in Equations (14.9) and (14.10), and one obtains, analogously to Equation (13.42), a *virial expansion of the equation of state of the*

Fermi gas:

$$\frac{pV}{NkT} = \sum_{l=1}^{\infty}(-1)^{l-1}a_l x^{l-1} \qquad \text{with} \qquad x = \frac{\lambda^3}{gv} = \frac{N\lambda^3}{gV} \tag{14.37}$$

The coefficients a_l are here the same as in Equation (13.43), only the signs are changed.

The degenerate Fermi gas

We now want to study the other limiting case, when temperatures are low and densities high. The extreme case $T = 0$ is now of special interest, because in many quantum mechanical (e.g., atomic) systems the typical excitation energies are larger than a few tenths of eV. The mean thermal energy at room temperature, however, is only approximately $\frac{1}{40}$ eV; i.e., it is far less than what is required for excitations, so that for such systems (e.g., an electron gas in a metal) room temperature is nearly the same as $T = 0$.

In this case, the mean occupation number $\langle n_k \rangle^{\text{FD}}$ is in good approximation described by the step function $\Theta(\mu - \epsilon)$. The functions $f_n(z)$ may in this case be approximated by Equation (14.26). One thus has for Equations (14.9) and (14.10)

$$\frac{p}{kT} \approx \frac{g}{\lambda^3}\left(\frac{\mu}{kT}\right)^{5/2}\frac{1}{\Gamma\left(\frac{7}{2}\right)} \qquad \text{or} \qquad p \approx g\left(\frac{2\pi m}{h^2}\right)^{3/2}\mu^{5/2}\frac{8}{15\sqrt{\pi}} \tag{14.38}$$

$$\frac{N}{V} \approx \frac{g}{\lambda^3}\left(\frac{\mu}{kT}\right)^{3/2}\frac{1}{\Gamma\left(\frac{5}{2}\right)} \qquad \text{or} \qquad \frac{N}{V} \approx g\left(\frac{2\pi m}{h^2}\right)^{3/2}\mu^{3/2}\frac{4}{3\sqrt{\pi}} \tag{14.39}$$

This limit can also be derived directly. In the case $T = 0$, the mean occupation number $\langle n_\epsilon \rangle^{\text{FD}}$ is given by

$$\langle n_\epsilon \rangle^{\text{FD}}_{T=0} = \Theta(\mu - \epsilon) = \begin{cases} 1 & \text{if } \epsilon \leq \mu \\ 0 & \text{if } \epsilon > \mu \end{cases} \tag{14.40}$$

For $T = 0$ the chemical potential μ must be identified with the Fermi energy ϵ_f of the system (the energy of the highest occupied state). The particle number and the internal energy can be calculated directly using Equation (14.40):

$$\begin{aligned} N &= \int_0^\infty d\epsilon\, g(\epsilon)\Theta(\mu - \epsilon) \\ &= g\frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\mu \epsilon^{1/2}\,d\epsilon \\ &= gV\left(\frac{2\pi m}{h^2}\right)^{3/2}\frac{4}{3\sqrt{\pi}}\mu^{3/2} \end{aligned} \tag{14.41}$$

$$U = \int_0^\infty d\epsilon\, g(\epsilon)\Theta(\mu - \epsilon)\epsilon$$

$$= g\frac{2\pi V}{h^3}(2m)^{3/2}\int_0^{\mu}\epsilon^{3/2}\,d\epsilon$$

$$= gV\left(\frac{2\pi m}{h^2}\right)^{3/2}\frac{4}{5\sqrt{\pi}}\mu^{5/2} \tag{14.42}$$

which agrees exactly with Equations (14.38) and (14.39) because of Equation (14.30). Dividing Equation (14.42) by Equation (14.41), one obtains

$$\frac{U}{N} = \frac{3}{5}\mu, \qquad \text{with} \quad \mu = \epsilon_f \text{ for } T = 0 \tag{14.43}$$

The mean energy per particle is given by 3/5 of the Fermi energy. From Equation (14.41) one calculates

$$\epsilon_f = \mu = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{g}\frac{N}{V}\right)^{2/3}$$

and

$$\frac{U}{V} = \frac{3}{2}p = \frac{3}{5}\left(\frac{6\pi^2}{g}\right)^{2/3}\frac{\hbar^2}{2m}\left(\frac{N}{V}\right)^{5/3} \tag{14.44}$$

i.e., the energy density is proportional to the five-thirds power of the particle density. In the following we calculate corrections to this limit for small, but nonvanishing temperatures. To this end, we retain the next terms in the expansions for the $f_n(z)$ for $z \gg 1$:

$$f_{5/2}(z) \approx \frac{8}{15\sqrt{\pi}}(\ln z)^{5/2}\left(1 + \frac{5\pi^2}{8}(\ln z)^{-2} + \cdots\right)$$

$$f_{3/2}(z) \approx \frac{4}{3\sqrt{\pi}}(\ln z)^{3/2}\left(1 + \frac{\pi^2}{8}(\ln z)^{-2} + \cdots\right)$$

$$f_{1/2}(z) \approx \frac{2}{\sqrt{\pi}}(\ln z)^{1/2}\left(1 - \frac{\pi^2}{24}(\ln z)^{-2} + \cdots\right) \tag{14.45}$$

At first we have again to determine z from Equation (14.10):

$$\frac{N}{V} = \frac{4\pi g}{3}\left(\frac{2m}{h^2}\right)^{3/2}(kT\ln z)^{3/2}\left(1 + \frac{\pi^2}{8}(\ln z)^{-2} + \cdots\right) \tag{14.46}$$

This expression is now to be (approximately) solved for z. Here we take advantage of the fact that the second term in the last bracket is already small. Therefore, we may insert in this term the zeroth approximation for z. This was

$$kT\ln z = \mu = \left(\frac{3N}{4\pi gV}\right)^{2/3}\frac{h^2}{2m} = \epsilon_f \tag{14.47}$$

and we obtain as a better approximation:

$$kT\ln z = \mu \approx \epsilon_f\left(1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_f}\right)^2\right) \tag{14.48}$$

With increasing temperature the chemical potential decreases. The expansion parameter is here the ratio of thermal excitation energy kT to the Fermi energy of the system. For the internal energy we now find

$$\frac{U}{N} = \frac{3}{2}kT\frac{f_{5/2}(z)}{f_{3/2}(z)} \approx \frac{3}{2}kT\frac{2}{5}\ln z\frac{\left(1+\frac{5\pi^2}{8}(\ln z)^{-2}+\cdots\right)}{\left(1+\frac{\pi^2}{8}(\ln z)^{-2}+\cdots\right)} \tag{14.49}$$

If one expands the denominator as $(1+\alpha)^{-1} \approx 1-\alpha$, it follows that

$$\frac{U}{N} \approx \frac{3}{5}kT\ln z\left(1+\frac{\pi^2}{2}(\ln z)^{-2}+\cdots\right) \tag{14.50}$$

Finally, one can also insert Equation (14.48) for $\ln z$:

$$\frac{U}{N} \approx \frac{3}{5}\epsilon_f\left(1+\frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_f}\right)^2+\cdots\right) \tag{14.51}$$

The internal energy of a Fermi system does not approach zero for low temperatures, as does that of a classical ideal gas or of the ideal Bose gas; rather, it converges toward a finite value, which is given by the total energy of the states occupied at $T = 0$, (which is finite, because of the Pauli principle). The specific heat can be immediately calculated with the help of Equation (14.51):

$$\frac{C_V}{Nk} = \frac{1}{Nk}\left.\frac{\partial U}{\partial T}\right|_{V,N} = \frac{\pi^2}{2}\frac{kT}{\epsilon_f}+\cdots \tag{14.52}$$

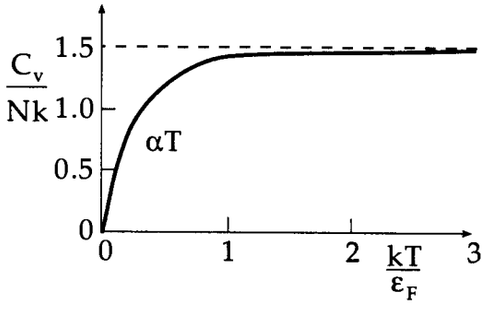


Figure 14.2. Specific heat of the Fermi gas.

The specific heat of the Fermi gas is shown in Figure 14.2. Equation (14.52) means in particular that for $kT \ll \epsilon_f$ the specific heat increases linearly, and that it vanishes for $T = 0$. Thus we can now understand why, for instance, electrons in metals or solids do not contribute to the specific heat at room temperature, which was a large problem of classical statistical mechanics.

According to the classical theory, *all* degrees of freedom of a system should contribute, on average, $\frac{1}{2}kT$ to the internal energy and $\frac{1}{2}k$ to the specific heat.

We were able to prove this for rotations and vibrations in polyatomic molecules (at least for high temperatures). However, the electrons, and even more so, the constituents of the nuclei, do not contribute to the specific heat since their Fermi energy is very high. Thus, electronic excitations are not found at temperatures below several hundred or thousand K, while nuclear excitations require even much higher temperatures.

However, this general statement requires some caution. At very low temperatures the specific heat is very small ($C_V \to 0$), but the contribution of the electrons grows linearly with temperature, while the otherwise dominant contribution of the phonons converges towards zero as T^3. Thus, at very small temperatures the main contribution to the specific heat stems nevertheless from the electrons and not from the phonons. For low temperatures

the specific heat should therefore become a superposition of a T-dependence and a T^3-dependence,

$$C_V \approx \alpha T + \gamma T^3 \tag{14.53}$$

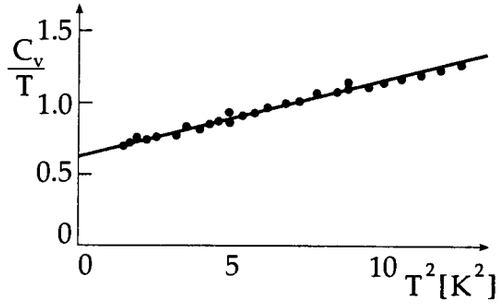


Figure 14.3. Specific heat of copper.

One can compare this prediction with experiment. To this end, one plots the measured data in the form C_V/T versus T^2, which should give a straight line for $T \to 0$. As one observes in Figure 14.3, the prediction is in excellent agreement with experiment. The contribution of the electrons can be directly read off by extrapolating the straight line to $T = 0$.

For metals, α is of the order 0.8 mJ $\text{mol}^{-1}\text{°K}^{-2}$. For salts like KCl, however, α is much smaller, since the electrons in salts cannot be described by a free electron gas. Many other properties of metals were only understood with the realization that electrons in a metal behave approximately as a free Fermi gas at temperature $T = 0$ (one also calls this gas a *degenerate Fermi gas*). Such properties include good heat conductivity and good electrical conductivity, as well as the temperature dependence of these quantities.

The degenerate Fermi gas also plays an important role in nuclear physics and astronomy; we will get acquainted with the corresponding examples later on.

Finally, for the sake of completeness we want to denote the free energy $F = \mu N - pV$ and the entropy $S = \frac{1}{T}(U - F)$ in terms of the expansion $kT \ll \epsilon_f$:

$$\frac{F}{N} = \frac{3}{5}\epsilon_f \left(1 - \frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_f}\right)^2 + \cdots\right) \tag{14.54}$$

$$\frac{S}{Nk} = \frac{\pi^2}{2}\frac{kT}{\epsilon_f} \tag{14.55}$$

Especially, $S \to 0$ for $T \to 0$. The degenerate Fermi gas at $T = 0$ represents, just as the Bose condensate, the state of the system with the highest degree of order.

Example 14.1: Richardson effect, thermionic emission

The model of an ideal Fermi gas for the electrons in the conduction band of metals allows us to calculate some interesting measurable quantities, for instance the dependence of the emission current density from a hot cathode on temperature and the work function. The latter is defined as the amount of energy necessary to remove one electron from the metal. One can think of the metal as a potential well of depth W, in which the electrons are allowed to move freely (see Figure 14.4). The difference between the bottom of the well and the Fermi energy at $T = 0$ is the work function ϕ. If the gas is heated up, electrons will also occupy higher states according to the Fermi–Dirac distribution of the mean occupation number.

In particular, we want to assume that all electrons which hit a surface area element dA_z with momentum p_z and fulfill the requirement $\epsilon_z = p_z^2/2m \geq W$ can leave the metal,

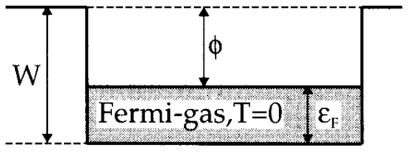


Figure 14.4. Form of the potential.

independent of their momentum components parallel to the surface element. In analogy to Exercise 7.6, the rate of emission of these electrons, R, is given by

$$R = \frac{d^2N}{dA\,dt} = \frac{2}{h^3}\int_{-\infty}^{+\infty} dp_x \int_{-\infty}^{+\infty} dp_y \int_{\sqrt{2mW}}^{\infty} dp_z \frac{p_z}{m} \langle n_p \rangle^{\text{FD}} \tag{14.56}$$

where we have used the mean occupation number $\langle n_p \rangle$ of the momentum state $\vec{p}$ instead of a velocity distribution. This is normalized to N and not to 1, like $f(\vec{v})$. Furthermore, the number of quantum mechanical momentum states in the momentum interval $d^3\vec{p}$ is, for large volumes, given by

$$\frac{2}{h^3} d^3\vec{p} \int d^3x = \frac{2V}{h^3} d^3\vec{p}$$

where the factor 2 takes into account the degeneracy of the momentum states with respect to the spin projections of the electrons. If one lumps everything together, Equation (14.56) follows from Equation (7.68). The Fermi–Dirac distribution is

$$\langle n_p \rangle^{\text{FD}} = \frac{1}{\exp\left\{\beta\left(\frac{p^2}{2m} - \mu\right)\right\} + 1}$$

The integrals over p_x and p_y in Equation (14.56) can be performed if one introduces plane polar coordinates $p_x = p\cos\phi$, $p_y = p\sin\phi$, and $dp_x\,dp_y = p\,dp\,d\phi$ (note that $p \neq |\vec{p}| = \sqrt{p_x^2 + p_y^2 + p_z^2}$, but that $p = \sqrt{p_x^2 + p_y^2}$). The angular integral yields, of course, only the factor 2π, and one obtains

$$R = \frac{4\pi}{mh^3}\int_{\sqrt{2mW}}^{\infty} dp_z \int_0^{\infty} p\,dp \frac{p_z}{\exp\left\{\frac{p^2}{2mkT} + \frac{p_z^2}{2mkT} - \frac{\mu}{kT}\right\} + 1}$$

$$= \frac{4\pi kT}{h^3}\int_{\sqrt{2mW}}^{\infty} dp_z p_z \ln\left[1 + \exp\left\{-\frac{p_z^2}{2mkT} + \frac{\mu}{kT}\right\}\right] \tag{14.57}$$

where we have also used

$$\frac{d}{dx}\ln[1 + e^x] = \frac{e^x}{1 + e^x} = \frac{1}{e^{-x} + 1}$$

with $x = -(p^2/2m + p_z^2/2m - \mu/kT)$. If one substitutes $\epsilon = p_z^2/2m$ into Equation (14.57), it follows that

$$R = \frac{4\pi mkT}{h^3}\int_W^{\infty} d\epsilon \ln\left[1 + \exp\left\{\frac{\mu - \epsilon}{kT}\right\}\right] \tag{14.58}$$

Now we can show for the electron gas in metals that the term $\exp\{(\mu - \epsilon)/kT\}$ is very small for temperatures up to 2000 K. The difference $\mu - \epsilon$ is at most of the order $\epsilon_f - W = -\phi$. In general, $(-\phi)$ is negative and of the order of eV, which is consistent, because $k \approx 1\,\text{eV}/12000\,\text{K}$ up to temperatures of 12000 K. Then, however, one may in any case expand the logarithm in Equation (14.58) ($\ln(1 + x) \approx x$), and one finds

$$R = \frac{4\pi mkT}{h^3}\int_W^{\infty} d\epsilon \exp\left\{\frac{\mu - \epsilon}{kT}\right\} = \frac{4\pi m(kT)^2}{h^3}\exp\left\{\frac{\mu - W}{kT}\right\} \tag{14.59}$$

By the way, one easily proves that this result for R agrees with the classical result, if one inserts the Maxwell–Boltzmann distribution into Equation (14.56) instead of the Fermi–Dirac distribution. The reason is that the approximation (14.58) $\rightarrow$ (14.59) corresponds to the Boltzmann limit. Nevertheless, there is a difference in the current densities. In the classical Boltzmann limit the temperature dependence of the chemical potential was

$$z = \exp\left\{\frac{\mu}{kT}\right\} = \frac{n\lambda^3}{g} = \frac{N}{gV}\frac{h^3}{(2\pi mkT)^{3/2}} \qquad (kT \gg \epsilon_f)$$

where we have to assume $kT \gg \epsilon_f$, while in the correct quantum mechanical case $\mu \approx \epsilon_f$ is nearly temperature independent because of the degeneracy of the Fermi gas of electrons ($kT \ll \epsilon_f$),

$$z = \exp\left\{\frac{\mu}{kT}\right\} = \exp\left\{\frac{\epsilon_f}{kT}\right\} \qquad (kT \ll \epsilon_f)$$

Thus, the classical current density (for electrons with $g = 2$) reads

$$J_{\text{class}} = eR = \frac{N}{V} e \left(\frac{kT}{2\pi m}\right)^{1/2} \exp\left\{-\frac{W}{kT}\right\} \tag{14.60}$$

and the work function ϕ agrees with the bottom of the well in the classical case. On the other hand, with the correct value of the chemical potential, $\mu = \epsilon_f$, it follows that

$$J_{qm} = eR = \frac{4\pi me}{h^3}(kT)^2 \exp\left\{-\frac{\phi}{kT}\right\} \tag{14.61}$$

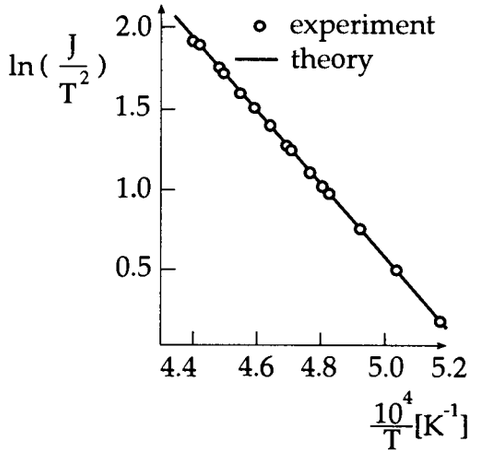


Figure 14.5. Comparison between experiment and theory of the Richardson effect.

i.e., the correct value for the work function, $\phi = W - \epsilon_f$. In particular, the temperature dependence is different in both cases. If one plots $\ln(J/T^2)$ versus $1/T$, according to Equation (14.61), a straight line should result, which is confirmed by experiment, in contradiction to Equation (14.60). (See Figure 14.5.) It is very interesting that one may not treat the effusion of electrons out of the metal in the Boltzmann approximation (even if the rate R formally agrees in both cases, but not the chemical potential), but that in equilibrium (without an external potential, which exhausts the electrons) a cloud of electrons will form around the metal which may be treated classically, since the electron density inside will be in general very small.

The rate of electrons returning into the metal will then be (as in Exercise 7.6):

$$R' = \frac{1}{4}\frac{N}{V}\langle v\rangle = \frac{1}{4}\frac{p}{kT}\left(\frac{8kT}{\pi m}\right)^{1/2} = \frac{p}{(2\pi mkT)^{1/2}} \tag{14.62}$$

where the charge cloud may now be treated as a classical ideal gas. On the other hand, the pressure p of a classical ideal gas of electrons is, according to Example 9.1, given by

$$p = 2kT\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \exp\left\{\frac{\mu'}{kT}\right\} \tag{14.63}$$

where the additional factor 2 originates from the degeneracy of the electrons (cf., also Equation (14.9) for $z \ll 1$). However, the chemical potential μ' of the charge cloud is shifted by W

against that of the electrons in the metal, since the zero points of the energy scale are shifted by this value. With $\mu' = \mu - W$ it follows from Equations (14.62) and (14.63) that

$$R' = \frac{4\pi m}{h^3}(kT)^2 \exp\left\{\frac{\mu - W}{kT}\right\} \tag{14.64}$$

The rates of effusion from the metal (14.59) and the return rate (14.64) thus agree, as it should be in thermodynamic equilibrium. However, while the electrons in the interior of the metal are strongly degenerate and have to obey Fermi–Dirac statistics, the charge cloud around the metal may be treated in the Boltzmann limit.

Exercise 14.2: Hallwachs effect, photoelectric emission

Calculate the current density of electrons emerging from a metal of temperature T, which is illuminated with short wavelength radiation. Use the same model of the metal as in the preceding example and assume that a metal electron, which scatters with a photon of energy $\hbar\omega$, obtains this amount of energy as additional kinetic energy.

Solution

An electron in the metal, which scatters from an incoming photon, can absorb the whole energy of the photon, since there are enough other particles present, for instance atoms, to absorb the recoil (momentum balance). Such an electron can leave the metal in z–direction, if the condition

$$\frac{p_z^2}{2m} + \hbar\omega > W \qquad \text{or} \qquad \frac{p_z^2}{2m} > W - \hbar\omega$$

is fulfilled. Thus we can continue, as for the Richardson effect, using a potential depth which is reduced by $\hbar\omega$. Equation (14.58) now becomes

$$R = \frac{4\pi mkT}{h^3}\int_{W-\hbar\omega}^{\infty} d\epsilon \ln\left[1 + \exp\left\{\frac{\mu - \epsilon}{kT}\right\}\right] \tag{14.65}$$

R is now, however, only the rate of the scattered electrons which can leave the metal. The number of scattering processes per time interval increases proportionally to the intensity of the incoming radiation.

Now in Equation (14.65), one must not assume $\exp\{\beta(\mu - \epsilon)\} \ll 1$, since $W - \hbar\omega$ may actually be on the order of $\mu = \epsilon_f$. To evaluate the integral nevertheless, we substitute $x = \beta(\epsilon - W + \hbar\omega)$ and obtain

$$R = \frac{4\pi m}{h^3}(kT)^2 \int_0^{\infty} dx \ln[1 + \exp\{\beta\hbar(\omega - \omega_0) - x\}]$$

The expression $\hbar\omega_0 = W - \mu \approx W - \epsilon_f = \phi$ yields the frequency of the radiation corresponding to the work function ϕ. The current density becomes, with the abbreviation $\delta = \beta\hbar(\omega - \omega_0)$,

$$J = eR = \frac{4\pi me}{h^3}(kT)^2 \int_0^{\infty} dx \ln[1 + \exp\{\delta - x\}]$$

Here we integrate by parts, with the result

$$J = eR = \frac{4\pi me}{h^3}(kT)^2 \int_0^{\infty} dx \frac{x}{\exp\{x - \delta\} + 1}$$

This integral is just the standard function $f_2(e^\delta)$,

$$J = eR = \frac{4\pi me}{h^3}(kT)^2 f_2(e^\delta) \tag{14.66}$$

As already mentioned, the total current density is in addition proportional to the intensity of the radiation, where the reflecting power of the metal surface and the cross section of the scattering process enter the constant of proportionality.

We first investigate Equation (14.66) in the limit $\hbar(\omega - \omega_0) \gg kT$ (ultraviolet, X-ray). In this case $e^\delta \gg 1$, and one may approximate the function $f_2(e^\delta)$ for large arguments as $f_2(e^\delta) \approx \frac{1}{2}\delta^2$. Hence we obtain

$$J \approx \frac{me}{2\pi h}(\omega - \omega_0)^2 \qquad \text{for} \qquad \hbar(\omega - \omega_0) \gg kT$$

This result is independent of temperature, since the thermal excitation does not contribute to the emission at small temperatures.

On the other hand, we can also evaluate Equation (14.66) for long wavelength radiation $\omega < \omega_0$, with $\hbar|\omega - \omega_0| \gg kT$. Then $e^\delta \ll 1$ and $f_2(e^\delta) \approx e^\delta$. It follows that

$$J \approx \frac{4\pi me}{h^3}(kT)^2 \exp\left\{\frac{\hbar\omega - \phi}{kT}\right\}$$

This corresponds to pure thermal emission with the work function decreased by $\hbar\omega$. Finally we can also consider the special case $\hbar\omega = \hbar\omega_0$, i.e., the case where the radiation just provides the work function. With $e^\delta = 1$ one finds $f_2(1) = \frac{1}{2}\zeta(2) = \pi^2/12$, and furthermore

$$J_0 = \frac{\pi^3 me}{3h^3}(kT)^2$$

i.e., even at the so-called threshold energy $\hbar\omega = \hbar\omega_0 = \phi$ the current is appreciably different from zero due to thermal excitation.

Exercise 14.3: Schottky effect

Estimate the influence of a constant electric field (perpendicular to the metal surface) on the rate of the thermionic emission and calculate the effective decrease of the work function (classically).

Hint: The difference between the potential energies of an electron at the distance z from the surface of the metal and an electron inside the metal is (Figure 14.6):

$$\Delta V(z) = W - e|\vec{E}|z - \frac{e^2}{4z} \tag{14.67}$$

(Reason?)

Solution

Due to the external electric field, the barrier to be overcome by the electrons is effectively lowered. The constant field with strength $\vec{E}$ in the $-z$–direction is described by a potential $-e|\vec{E}|z$, which additionally acts on the electrons (but only outside the metal). Moreover, the attractive force between the electrons which have left the metal and the positive residual charge of the metal has to be taken into account. In a crude approximation, this residual charge can be thought to be positioned at $-z$ inside the metal, if the electron is at $+z$ (induced mirror charge). This leads to a Coulomb force $-e^2/(2z)^2$ with the corresponding potential $e^2/4z$. An electron outside the metal has the potential energy $-e|\vec{E}|z - e^2/4z$. An electron inside

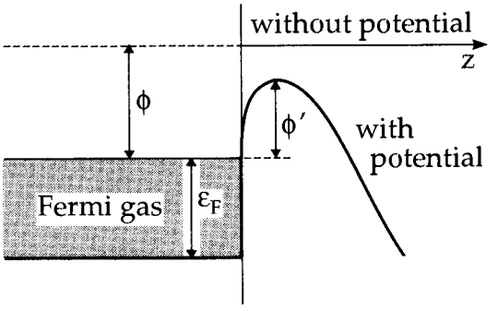


Figure 14.6. Potential in the vicinity of the metal surface (schematically). The metal surface is located at $z = 0$.

the metal, however, sitting in a potential well of depth W, has the potential energy $-W$. This leads to the potential difference (14.67). It is smaller than the original potential difference $\Delta V = W$ in the absence of the field.

To remove one electron from the metal we now have to add just enough energy to overcome the potential barrier (14.67). To this end, we determine the maximum height:

$$\left.\frac{\partial \Delta V}{\partial z}\right|_{z_{\max}} = 0 \Rightarrow -e|\vec{E}| + \frac{e^2}{4z_{\max}^2} = 0$$

or

$$z_{\max} = \sqrt{\frac{e}{4|\vec{E}|}}$$

Consequently,

$$\Delta V_{\max} = W - e^{3/2}|\vec{E}|^{1/2}, \qquad \text{and} \qquad \phi' = \Delta V_{\max} - \epsilon_f = \phi - e^{3/2}|\vec{E}|^{1/2}$$

is the effective work function, which is reduced compared to ϕ. If we insert this into the current density (14.61), we have

$$J_E = \frac{4\pi me}{h^2}(kT)^2 \exp\left\{-\beta\left(\phi - e^{3/2}|\vec{E}|^{1/2}\right)\right\} \tag{14.68}$$

or

$$J_E = J_0 \exp\left\{\beta e^{3/2}|\vec{E}|^{1/2}\right\}$$

Also, this dependence of the current density on an external field is well confirmed experimentally, although we have performed only a very crude estimate (no tunneling effects). The formula (14.68) must not be applied for large field strengths $|\vec{E}| > 10^8\ \mathrm{Vm}^{-1}$, since then cold emission and tunneling of the electrons become more and more important.

Example 14.4: Relativistic Fermi gas at $T = 0$

We want to derive the thermodynamic properties of a relativistic Fermi gas at temperature $T = 0$. As usual, we start from the logarithm of the grand partition function:

$$\ln \mathcal{Z} = \sum_k \ln(1 + z\exp\{-\beta\epsilon_k\})$$

The one-particle energies ϵ_k in the momentum state k are now taken to be relativistic, and we subtract the rest mass of the particles (cf. Chapter 8), to yield an easier check of the nonrelativistic limit,

$$\epsilon = mc^2\left[\sqrt{1 + \left(\frac{p}{mc}\right)^2} - 1\right] \tag{14.69}$$

Next we write the sum over all one-particle states as an integral over all momenta (cf. Equation (13.5), large volume)

$$\ln \mathcal{Z} = g \frac{4\pi V}{h^3} \int_0^\infty p^2\, dp \ln(1 + z \exp\{-\beta\epsilon\})$$

The logarithm can be removed by integrating by parts,

$$\ln \mathcal{Z} = g \frac{4\pi V}{h^3} \frac{\beta}{3} \int_0^\infty p^3\, dp \frac{d\epsilon}{dp} \frac{1}{z^{-1} \exp\{\beta\epsilon\} + 1}$$

The fugacity $z = \exp\{\beta\mu\}$ is to be determined for given particle number from

$$N(T, V, z) = \sum_k \langle n_k \rangle^{\mathrm{FD}} = g \frac{4\pi V}{h^3} \int_0^\infty p^2\, dp \frac{1}{z^{-1} \exp\{\beta\epsilon\} + 1}$$

We now want to consider the case $T = 0$. Then the mean occupation number has a simple form, $\langle n_\epsilon \rangle^{\mathrm{FD}} = \Theta(\epsilon_f - \epsilon)$, and thus it holds that

$$\ln \mathcal{Z} = g \frac{4\pi V}{h^3} \frac{\beta}{3} \int_0^{p_f} p^3\, dp \frac{d\epsilon}{dp} \tag{14.70}$$

$$N(T, V, z) = g \frac{4\pi V}{h^3} \int_0^{p_f} p^2\, dp = g \frac{4\pi V}{3h^3} p_f^3 \tag{14.71}$$

Here p_f is the momentum corresponding to the Fermi energy ϵ_f according to Equation (14.69), which can be determined from the particle density with the help of Equation (14.71):

$$p_f = \left(\frac{3}{4\pi} \frac{Nh^3}{Vg} \right)^{1/3} \tag{14.72}$$

Thus p_f is proportional to $n^{1/3}$ ($n = N/V$). This corresponds, of course, to the determination of the chemical potential $\mu = \epsilon_f = \epsilon_f(p_f)$ from the particle number and volume at $T = 0$. We now require $d\epsilon/dp$ for Equation (14.70):

$$\frac{d\epsilon}{dp} = c \frac{\left(\frac{p}{mc}\right)}{\left[1 + \left(\frac{p}{mc}\right)^2\right]^{1/2}}$$

If we insert this into Equation (14.70) and consider $\ln \mathcal{Z} = \mathcal{P}V/kT$, it follows that (we write here $\mathcal{P}$ for the pressure to avoid confusion with the momentum)

$$\mathcal{P} = \frac{4\pi g}{3h^3} \int_0^{p_f} mc^2 \frac{\left(\frac{p}{mc}\right)^2}{\left[1 + \left(\frac{p}{mc}\right)^2\right]^{1/2}} p^2\, dp \tag{14.73}$$

Before evaluating this integral, we also want to present an explicit expression for the energy. This is simpler than differentiating the partition function afterwards:

$$U = \sum_k \epsilon_k \langle n_k \rangle$$

$$= \frac{4\pi g V}{h^3} \int_0^{p_f} p^2\, dpmc^2 \left(\left[1 + \left(\frac{p}{mc} \right)^2 \right]^{1/2} - 1 \right) \qquad \text{for} \qquad T = 0 \tag{14.74}$$

To calculate the integrals (14.73) and (14.74), we make a substitution which is often useful in the relativistic case, $p = mc \sinh x$. Then we have $\epsilon = mc^2(\cosh x - 1)$ and $d\epsilon/dp = c \tanh x$.

If we finally set $p_f = mc \sinh x_f$, the following integrals have to be performed

$$\mathcal{P} = \frac{4\pi g m^4 c^5}{3h^3} \int_0^{x_f} \sinh^4 x \, dx \tag{14.75}$$

$$U = \frac{4\pi g V m^4 c^5}{h^3} \int_0^{x_f} (\cosh x - 1) \sinh^2 x \cosh x \, dx \tag{14.76}$$

These integrals are quite simple, if we use the properties of the hyperbolic functions:

$$\cosh^2 x - \sinh^2 x = 1$$

$$\cosh 2x = \cosh^2 x + \sinh^2 x$$

$$\sinh 2x = 2 \sinh x \cosh x$$

$$\frac{d}{dx} \sinh x = \cosh x$$

$$\frac{d}{dx} \cosh x = \sinh x$$

For example, we have

$$\begin{aligned} \sinh^4 x &= \sinh^2 x (\cosh^2 x - 1) = \frac{1}{4} \sinh^2 2x - \sinh^2 x \\ &= \frac{1}{8} \cosh 4x - \frac{1}{2} \cosh 2x + \frac{3}{8} \\ &= \frac{d}{dx} \left(\frac{1}{32} \sinh 4x - \frac{1}{4} \sinh 2x + \frac{3}{8} x \right) \end{aligned}$$

With this, Equation (14.75) can be immediately integrated. Analogously, one finds

$$\begin{aligned} \cosh^2 x \sinh^2 x - \sinh^2 x \cosh x &= \frac{1}{4} \sinh^2 2x - \sinh^2 x \cosh x \\ &= \frac{1}{8} \cosh 4x - \frac{1}{8} - \sinh^2 x \frac{d \sinh x}{dx} \\ &= \frac{d}{dx} \left(\frac{1}{32} \sinh 4x - \frac{x}{8} - \frac{1}{3} \sinh^3 x \right) \end{aligned}$$

namely, exactly the integrand (14.76). One can again transform the results of the integration (hyperbolic functions of multiples of the argument) into hyperbolic functions of the argument alone:

$$\int_0^{x_f} \sinh^4 x \, dx = \frac{1}{8} \left(3x_f - 3 \sinh x_f \cosh x_f + 2 \sinh^3 x_f \cosh x_f \right) \tag{14.77}$$

$$\begin{aligned} &\int_0^{x_f} (\cosh x - 1) \sinh^2 x \cosh x \, dx \\ &\quad = \frac{1}{8} \left(-x_f + \sinh x_f \cosh x_f + 2 \sinh^3 x_f \cosh x_f - \frac{8}{3} \sinh^3 x_f \right) \end{aligned} \tag{14.78}$$

We now introduce, for sake of abbreviation, two functions $A(y)$ and $B(y)$ (Figure 14.7):

$$y = \sinh x = \frac{p}{mc} \qquad \text{and} \qquad y_f = \sinh x_f = \frac{p_f}{mc} \tag{14.79}$$

$$A(y) = \sqrt{1+y^2}(2y^3 - 3y) + 3\,\text{Arcsinh}\,y$$

$$B(y) = 8y^3(\sqrt{1+y^2} - 1) - A(y)$$

Then Equations (14.77) and (14.78) are much more conveniently expressed in the form:

$$\int_0^{x_f} \sinh^4 x\,dx = \frac{1}{8}A(y_f)$$

$$\int_0^{x_f} (\cosh x - 1)\sinh^2 x \cosh x\,dx = \frac{1}{24}B(y_f)$$

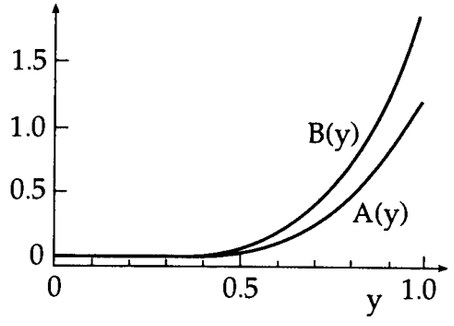


Figure 14.7. The functions $A(y)$ and $B(y)$.

We thus have the clear results

$$\mathcal{P} = \frac{g\pi m^4c^5}{6h^3}A(y_f) \qquad \textbf{(14.80)}$$

$$U = \frac{g\pi Vm^4c^5}{6h^3}B(y_f) \qquad \textbf{(14.81)}$$

with the dimensionless quantity y_f from Equation (14.79).

It is useful to investigate the nonrelativistic limit $y_f \ll 1$ and the ultrarelativistic limit $y_f \gg 1$. To this end, we need simply the respective expansions of the functions $A(y)$ and $B(y)$.

With arcsinh $y = \ln(y + \sqrt{1+y^2})$ one obtains

$$A(y) \approx \frac{8}{5}y^5 - \frac{4}{7}y^7 + \cdots \qquad y \ll 1 \qquad \textbf{(14.82)}$$

$$B(y) \approx \frac{12}{5}y^5 - \frac{3}{7}y^7 + \cdots \qquad y \ll 1 \qquad \textbf{(14.83)}$$

Also, for large arguments one may write down an expansion, if one writes $A(y) = 2y^4\sqrt{1+y^{-2}} - 3y^2\sqrt{1+y^{-2}} + 3\ln\left\{y(1+\sqrt{1+y^{-2}})\right\}$ and takes y^{-2} to be a small quantity,

$$A(y) \approx 2y^4 - 2y^2 + 3\ln 2y - \frac{7}{4} + \frac{5}{4}y^{-2} + \cdots \qquad \text{for} \quad y \gg 1 \qquad \textbf{(14.84)}$$

$$B(y) \approx 6y^4 - 8y^3 + 6y^2 - 3\ln 2y + \frac{3}{4} - \frac{3}{4}y^{-2} + \cdots \qquad \text{for} \quad y \gg 1 \qquad \textbf{(14.85)}$$

In the nonrelativistic case $y_f \ll 1$ we obtain from Equations (14.80) and (14.81) just the results (14.30) and (14.44) of the ideal Fermi gas, if we restrict ourselves to the lowest order approximation in Equation (14.82) and (14.83):

$$\mathcal{P} = \frac{g\pi m^4c^5}{6h^3}\frac{8}{5}\left(\frac{p_f}{mc}\right)^5 = \frac{2}{3}\left(\frac{2\pi g}{5h^3m}p_f^5\right) = \frac{2}{3}\frac{U}{V}$$

since

$$U = \frac{g\pi Vm^4c^5}{6h^3}\frac{12}{5}\left(\frac{p_f}{mc}\right)^5 = \frac{2\pi gV}{5h^3m}p_f^5$$

In the ultrarelativistic case $y_f \gg 1$, however, we get

$$\mathcal{P} = \frac{g\pi m^4c^5}{6h^3}2\left(\frac{p_f}{mc}\right)^4 = \frac{1}{3}\left(\frac{g\pi c}{h^3}p_f^4\right) = \frac{1}{3}\frac{U}{V}$$

since

$$U = \frac{g\pi V m^4 c^5}{6h^3} 6 \left(\frac{p_f}{mc}\right)^4 = \frac{g\pi V c}{h^3} p_f^4$$

which will be checked later in Example 14.11.

A main application of the cold relativistic Fermi gas arises in astrophysics. In 1930 Chandrasekhar found that stars which are called *white dwarfs* are very well described in the framework of this model system for electrons. In the following Exercise we want to investigate this in more detail.

Exercise 14.5: White dwarfs, supernovae, neutron stars, quark stars, and black holes

Consider the following model of a white dwarf: a gas sphere, consisting of helium, of mass $M \approx 10^{30}$ kg, at a density of $\rho = 10^{10}$ kg m^{-3} and a (central) temperature of $T = 10^7$ K (at these temperatures the helium atoms are nearly completely ionized).

1) Show that despite the large temperature the electron gas can be considered to be very cold ($kT \ll \epsilon_f$), but that on the other hand relativistic effects become important.

2) Show that the main contribution to the total pressure originates from free electrons, while the contribution of the helium nuclei is very small. Show in particular that the helium nuclei may be considered as a classical ideal gas.

3) Calculate the equilibrium radius of a white dwarf under the assumption that in equilibrium the pressure of the electrons just balances the gravitational pressure. Neglect here the radial change of density and pressure. Show that there is a relationship between the mass of the star and its radius, and investigate the limits of this relation.

4) What happens, if the mass of the star is 10–20 times larger?

Solution

We first estimate the Fermi energy and the Fermi momentum of the electrons in the gas with the help of the mass density ρ. Each ionized helium atom contributes two electrons and four nucleons to the total mass. The helium nuclei may be treated nonrelativistically, since their mean kinetic energy, due to the thermal energy $kT \approx 1$ keV, is very small compared to their rest mass $m_{\mathrm{He}}c^2 \approx 4$ GeV. Also, for the electrons, the contribution of the kinetic energy to the total mass is still rather small ($m_e c^2 \approx 511$ keV), so that we may write (if N denotes the number of electrons in the star),

$$M \approx N(m_e + 2m_n) \approx 2m_n N$$

since $m_e \ll m_n$ and since two nucleon masses belong to one electron. Therewith, the particle density of the electrons in the star may be estimated as

$$n = \frac{N}{V} \approx \frac{M/2m_n}{M/\rho} \approx \frac{\rho}{2m_n} \approx 3 \cdot 10^{36} \frac{\text{electrons}}{\text{m}^3} \approx 3 \cdot 10^{-9} \frac{\text{electrons}}{\text{fm}^3}$$

(1 fm $= 10^{-15}$ m). From this density we calculate for the Fermi momentum of the electrons, according to Equation (14.72):

$$p_f = \left(\frac{3n}{4\pi g}\right)^{1/3} h \approx 5 \cdot 10^{-22} \frac{\text{kg m}}{\text{s}} \approx 0.9 \frac{\text{MeV}}{c}$$

If we insert this into the relativistic energy–momentum relation, we obtain for the (kinetic) Fermi energy, without the rest mass of the electrons, $\epsilon_f \approx 0.5$ MeV. Thus, relativistic effects become important, but because $kT \approx 1$ keV $\ll \epsilon_f$, the electron gas may be considered as cold.

Second, for the helium nuclei we calculate the parameter $n\lambda^3$, which tells us whether quantum effects are important (cf. Chapter 13):

$$\lambda_{\mathrm{He}} = \left(\frac{h^2}{2\pi mkT} \right)^{1/2} \approx 247 \text{ fm}$$

Since the particle number density of the helium nuclei is half that of the electrons, it follows that $n\lambda_{\mathrm{He}}^3 \approx 2.27 \cdot 10^{-2}$, which is small compared to 1. Thus, we may apply the Boltzmann limit. The helium nuclei therefore contribute a pressure

$$p_{\mathrm{He}} = n_{\mathrm{He}} kT \approx 1.5 \cdot 10^{-12} \frac{\mathrm{MeV}}{\mathrm{fm}^3}$$

On the other hand, according to Equation (14.80), we find for the Fermi pressure of the electrons, with $y_f = p_f/mc \approx 2$ and with the function $A(y)$ introduced in the last example (which we here crudely approximate by its expansion for $y \gg 1$, i.e., $A(y_f) \approx A(2) \approx 26.7$:

$$p_e = \frac{1}{24\pi^2} \frac{(mc^2)^4}{(\hbar c)^3} \cdot 26.7 \approx 10^{-9} \frac{\mathrm{MeV}}{\mathrm{fm}^3}$$

which is 1000 times larger than the pressure of the helium nuclei.

Up to now, we have assumed that the gas is enclosed by a box. This is of course not the case, but gravity prevents the gas from leaking out. If the gas expands by a volume dV while the gas sphere is enlarged by dR, the energy

$$dE_p = -p\, dV = -p(R) 4\pi R^2\, dR$$

will be gained. However, the pressure is a function of the Fermi momentum (see Equation (14.80)), and the latter depends in turn on the volume or radius (at given particle number). On the other hand, when the sphere is enlarged the potential energy increases by the amount

$$dE_g = \frac{dE_g(R)}{dR} dR = \alpha \frac{GM^2}{R^2}\, dR \qquad \text{where} \qquad E_g(R) = -\alpha \frac{GM^2}{R} \tag{14.86}$$

The additional factor α stands for eventual corrections which result from an inhomogeneous density distribution. However, in the case considered here it is on the order of 1. In thermodynamic equilibrium, the free energy has to have a minimum; i.e., $dF = 0$. Since we consider the system at $T = 0$, it holds, with $F = E - TS = E$, that

$$dF = dE_g + dE_p = 0 = \alpha \frac{GM^2}{R^2} - p(R) 4\pi R^2$$

or

$$p(R) = \frac{\alpha}{4\pi} \frac{GM^2}{R^4} \tag{14.87}$$

A relationship between the mass and the radius of the star follows from this equation. If we insert Equation (14.80) for the pressure, and Equation (14.72) for the Fermi momentum, Equation (14.87) becomes

$$A \left(\left(\frac{9\pi M}{8m_n} \right)^{1/3} \frac{\hbar c}{m_e c^2} \frac{1}{R} \right) = 6\pi\alpha \left(\frac{\hbar c}{m_e c^2} \frac{1}{R} \right)^3 \frac{1}{m_e c^2} \frac{GM^2}{R} \tag{14.88}$$

The units in this equation for $R(M)$ are remarkable: the mass M of the star is measured in units of the nucleon mass m_n, and the radius R of the star in units of the Compton wavelength

of the electrons $\hbar c/m_e c^2$. Finally, the gravitational energy GM^2/R appears on the right-hand side, measured in units of the electron mass $m_e c^2$. Equation (14.88) thus relates quantum mechanics, special relativity, and classical gravitational theory. Unfortunately, it can be solved neither for $R(M)$ nor for $M(R)$. However, the limiting cases, where the argument of the function A becomes very large or very small, are analytically solvable. First we note that with $M \approx 10^{30}$ kg, $m_n \approx 1.6 \cdot 10^{-27}$ kg, $\hbar c = 197$ MeV fm, and $m_e c^2 \approx 0.5$ MeV, the argument of the function A is 1 if $R \approx 5 \cdot 10^6$ m. Therefore, for small arguments $y_f = p_f/mc \ll 1$ we have $R \gg 10^6$ m, and Equation (14.88) becomes, with $A(y) \approx \frac{8}{5} y^5$:

$$R \approx \frac{3(9\pi)^{2/3}}{40\alpha} \frac{\hbar^2}{G m_n^{5/3} m_e} M^{-1/3}$$

In the case of a large argument $y \gg 1$ (or $R \ll 10^6$ m), $A(y) \approx 2y^4 - 2y^2$, and one obtains

$$R \approx \frac{(9\pi)^{1/3}}{2} \frac{\hbar c}{m_e c^2} \left(\frac{M}{m_n}\right)^{1/3} \left(1 - \left(\frac{M}{M_0}\right)^{2/3}\right)^{1/2}$$

where we have used the abbreviation

$$M_0 = \frac{9}{64} \left(\frac{3\pi}{\alpha^3}\right)^{1/2} \left(\frac{\hbar c}{G m_n^2}\right)^{3/2} m_n$$

and also taken into account the second order terms in $A(y)$. For $M_0 < M$ there are no real solutions for R. As one observes, the radius of the star approaches zero, if M converges towards the (finite) mass M_0. Consequently, there are no white dwarfs with a mass larger than M_0. One calls M_0 the *Chandrasekhar limit*. Obviously, the Fermi pressure can no longer compensate the gravitational pressure of the star for $M > M_0$, and the collapse of the star is the consequence. However, for masses M in the vicinity of M_0, which yield very small white dwarfs, strong effects originating from general relativity occur. These can no longer be neglected if the radius of the star is of the order of the Schwarzschild radius $R_S = 2GM/c^2$.

The considerations presented here were worked out in detail by Chandrasekhar in the years 1931–1935. The first investigations concerning this subject were done by Fowler (1926), who realized that the Fermi gas in a white dwarf is completely degenerate (in analogy to the electron gas in metals), while the perception that a relativistic treatment is in order originates from Anderson (1929) and Stoner (1929–1930). The numerical value of the Chandrasekhar mass is $M_0 \approx 10^{30}$ kg.

The detailed studies of Chandrasekhar yielded

$$M_0 = \frac{5.75}{\mu_e^2} M_{\text{sun}}$$

where μ_e^2 takes care of the ionization degree of the He atoms (the number of free electrons per He nucleus). This is, to good approximation, $\mu_e \approx 2$, from which $M_0 \approx 1.44\, M_{\text{sun}}$ follows.

Thus, our sun lies in the range of possible white dwarfs. If it burns its hydrogen reserves to helium, it might become a white dwarf of radius 2700 km. In the meantime, however, other stages of star development have to be passed (e.g., red giant). The white dwarf radius has to be compared to the Schwarzschild radius of 3 km. In Figure 14.8, the relationship between R and M/M_0 is illustrated. The radius is given in units of a characteristic length, 3860 km, and the circles are drawn for a comparison of sizes of the respective stars.

If our sun were significantly heavier, e.g., $M \geq 10M_0 - 20M_0$, the following scenario would ensue: after burning of the hydrogen to ^{4}He another combustion stage would

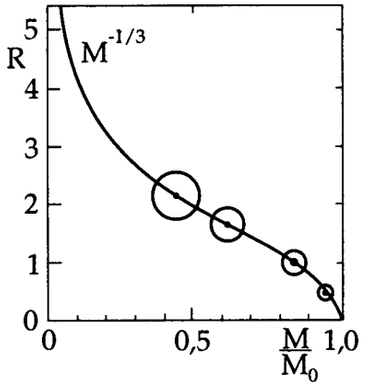


Figure 14.8. Numerical solution of Equation (14.88).

set in, where successively heavier nuclei (^{8}Be, ^{12}C, ^{16}O, ^{20}Ne, . . . , Si, . . . , Fe) with increasing binding energy per nucleon would be formed. However, if the core of the sun consisted of iron, the nuclear (binding) energy reserve would be exhausted: of all nuclei, iron binds the nucleons most strongly.*

A *supernova explosion* happens when the inner part of a star first collapses until very large densities $\rho \approx 10^{17}$ kg m^{-3} are obtained, comparable to atomic nuclei. This collapse happens in a very short time (about 1 millisecond). It produces a shock wave travelling outwards, which blasts off a part of the shell of the star into space—such a supernova was recently visible to the naked eye as a new, brightly shining star (in the great Magellanic cloud) in February 1987.

In the interior of such a star, at very high densities, most of the protons of the iron nuclei are transformed into neutrons and electrons under the influence of weak interactions. A (nearly) degenerate neutron gas is created, in which the Fermi pressure ($\approx$ GeV/c) now compensates the gravitational pressure: a *neutron star* has been formed.

Neutron stars already have been found experimentally; they are the so-called *pulsars*. However, there is again a maximum mass analogous to the Chandrasekhar mass, above which the gravitational pressure wins over. It is about 1.8 M_0.

If the star as it exists before the supernova explosion, the so-called progenitor sun, is too heavy, the Fermi pressure (and, at these densities, $> 10^{17}$ kg m^{-3}, the pressure due to the strong interaction between the neutrons) is not sufficient to stabilize the core of the neutron star – again gravitational collapse sets in: the matter of the star is compressed by the gravitational forces into a space region which is smaller than the volume given by the Schwarzschild radius and vanishes beyond the so-called "event horizon." Even photons may not escape from this collapsed star; a *black hole* is formed which is detectable by a distant observer only by its gravitational interaction (e.g., by the deviation of the light of other stars).

There are speculations that the mass limit for neutron stars is even larger, if quark matter is formed at high enough densities. Very little is known concerning the existence of such *quark stars*.

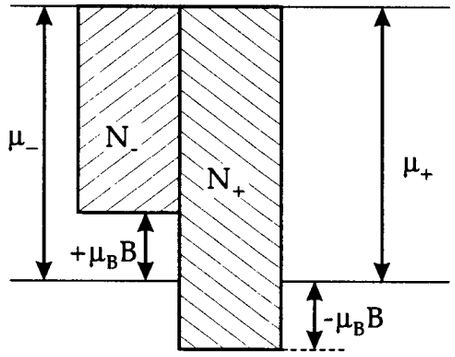
Example 14.6: Pauli paramagnetism

In this example we want to calculate the susceptibility of an ideal Fermi gas of N electrons (i.e., an electron gas in a metal) with magnetic moment $d_z = \gamma \mu_B m$, $m = \pm\frac{1}{2}$, $\gamma = 2$, in an external magnetic field for low temperatures ($kT \ll \epsilon_f$). Here we use $\vec{d}$ to denote the magnetic moment to avoid confusion with the chemical potential μ; $\mu_B = e\hbar/(2mc)$ is the Bohr magneton. We are mainly interested in deviations of the paramagnetic behavior from the classical Maxwell–Boltzmann limit (cf. Chapter 8).

To make the calculation as easy as possible, we neglect the influence of the external magnetic field on the wavefunctions of the electrons (see the following Example). Then, merely the energy of the free electrons

$$\epsilon = \frac{\vec{p}^2}{2m} - d_z B$$

*See for instance J. M. Eisenberg and W. Greiner, *Nuclear Theory I: Nuclear Models*, 3rd ed., North-Holland Amsterdam, 1988.



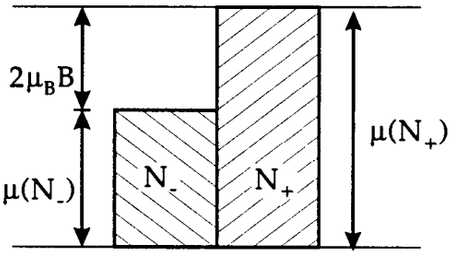


Figure 14.9. (left) Fermi gas with $B \neq 0$. (right) Figure 14.10. Two Fermi gases with $B = 0$.

changes (the magnetic field points in the z–direction). If the spin of the electron is parallel to the magnetic field ($m = +\frac{1}{2}$), the energy is decreased by $\mu_B B$; if it is antiparallel ($m = -\frac{1}{2}$), the energy is increased by $\mu_B B$. Thus the degeneracy of energy states with different spin projections, which is present in the case of vanishing external field, is removed. We can consider the system to be a mixture of two Fermi gases with $d_z = +\mu_B$ und $d_z = -\mu_B$, where N_+ electrons have $m = +\frac{1}{2}$ and N_- have $m = -\frac{1}{2}$ ($N_+ + N_- = N$). In a certain sense, these two gases can interact chemically with each other. Namely, the spin of an electron can flip, which corresponds to the reaction equation

$$e_\downarrow \rightleftharpoons e_\uparrow + \Delta E$$

if $\Delta E = 2\mu_B B$ is the required or emitted energy. From this we obtain, according to Equation (3.10), a condition for the chemical potentials μ_+ and μ_- of the two gases, which depend on the respective particle numbers N_+ and N_- (as well as on T and V):

$$\mu_+(N_+) = \mu_-(N_-) \tag{14.89}$$

On the other hand, the two gases are identical up to the energy shift with the ideal Fermi gas introduced in the beginning of this chapter (now the degeneracy is $g = 1$, since the magnetic field removes the spin degeneracy of the electrons). The chemical potentials $\mu_\pm$ can thus be expressed in terms of the chemical potential μ of a free Fermi gas:

$$\mu_+(N_+) = \mu(N_+) - \mu_B B$$

$$\mu_-(N_-) = \mu(N_-) + \mu_B B$$

since the energy scale of the two gases is simply shifted by $\pm\mu_B B$. The condition (14.89) can therefore be replaced by a condition for the chemical potentials of two free Fermi gases (with degeneracy factor $g = 1$ and particle numbers N_+, N_-),

$$\mu(N_+) - \mu(N_-) = 2\mu_B B \tag{14.90}$$

The advantage of this reinterpretation (Figures 14.9 and 14.10) is that we already know the chemical potentials in the case without a field. They have to be determined from the general equation ($g = 1$):

$$f_{3/2}(z) = \frac{N}{V}\lambda^3$$

with $z = \exp\{\beta\mu\}$, which yields the functions $\mu(N_+)$ and $\mu(N_-)$, if one inserts for n N_+ or N_-, respectively. Now $\mu_B = 0.578 \cdot 10^{-4}$ eV T^{-1}, and therefore even for strong magnetic

fields (several tens of thousands of Gauss or several Tesla) the magnetic energy $\mu_B B$ is small compared to the Fermi energy of a realistic electron gas in metals (several eV). According to the figures, the numbers N_+ and N_- are thus only slightly different from $N/2$ in the case without a field. Hence we set

$$N_+ = \frac{N}{2}(1+r)$$

$$N_- = \frac{N}{2}(1-r)$$

and consider r as a small parameter, with respect to which the chemical potentials $\mu(N_+)$ and $\mu(N_-)$ can expanded. Thus condition (14.90) becomes, via expansion with respect to r,

$$\mu\left(\frac{N}{2}(1+r)\right) - \mu\left(\frac{N}{2}(1-r)\right) \approx \left.\frac{\partial\mu(Nx)}{\partial x}\right|_{x=\frac{1}{2}} r = 2\mu_B B$$

From this equation one can determine the fraction r, and the particle numbers N_+ and N_- follow immediately. It is obvious that these are only mean particle numbers, since the actual particle numbers fluctuate due to the continuous spin–flip processes in the heat bath.

The total mean magnetic moment can be obtained via

$$\langle D_z\rangle = \mu_B(N_+ - N_-) = \mu_B N r = \frac{2\mu_B^2 B}{\mu'(\frac{N}{2})} \qquad \textbf{(14.91)}$$

since

$$\left.\frac{\partial\mu(Nx)}{\partial x}\right|_{x=\frac{1}{2}} = \mu'\left(\frac{N}{2}\right)\frac{\partial(Nx)}{\partial x} = \mu'\left(\frac{N}{2}\right)N$$

The mean magnetic moments in x– and y–directions vanish. From Equation (14.91) the susceptibility follows as

$$\chi = \lim_{B\to 0}\frac{\partial\langle D_z\rangle}{\partial B} = \frac{2\mu_B^2 N}{\mu'(\frac{N}{2})N} = \frac{2\mu_B^2}{\mu'(\frac{N}{2})} \qquad \textbf{(14.92)}$$

Thus, we only have to determine $\mu'(N/2)$. Unfortunately, this can be done analytically only for the limiting cases $kT \gg \epsilon_f$ (classical limit) and $kT \ll \epsilon_f$. For $T \to \infty$ we may use the approximation $f_{3/2}(z) \approx z - z^2/2^{3/2} + \cdots$. In first or second approximation, respectively, we obtain

$$z \approx \frac{N}{V}\lambda^3 \quad \text{or} \quad z \approx \frac{N}{V}\lambda^3\left(1 + \frac{N}{V}\frac{\lambda^3}{2^{3/2}}\right) \quad \text{for} \quad kT \gg \epsilon_f \qquad \textbf{(14.93)}$$

If one solves this for $\mu(N)$ and replaces N by Nx, the derivative (14.92) can be calculated,

$$\mu'\left(\frac{N}{2}\right)N = 2kT\left(1 + \frac{N}{V}\frac{\lambda^3}{2^{5/2}}\right) \quad \text{for} \quad kT \gg \epsilon_f$$

The susceptibility thus becomes

$$\chi \approx \chi_\infty\left(1 - \frac{n\lambda^3}{2^{5/2}}\right) \quad \text{with} \quad \chi_\infty = \frac{\mu_B^2 N}{kT} \quad \text{for} \quad kT \gg \epsilon_f$$

where $n = N/V$. The value of χ_∞ corresponds exactly to Equation (8.52), for $j = \frac{1}{2}$ (Curie law), which was formerly derived via classical Maxwell–Boltzmann statistics. For $kT \ll \epsilon_f$

we obtain, using Equation (14.48),

$$\mu(N) \approx \epsilon_f(N)\left(1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_f(N)}\right)^2\right)$$

$$\epsilon_f(N) = \left(\frac{3}{4\pi}\frac{N}{V}\right)^{2/3}\frac{h^2}{2m}$$

To calculate the Fermi energy we have to set $g = 1$, since we require $\epsilon_f(N)$ for the nondegenerate partial systems (N_+, N_-). To calculate the derivative (14.92), we consider

$$\left.\frac{\partial \epsilon_f(Nx)}{\partial x}\right|_{x=\frac{1}{2}} = \left.\frac{\partial}{\partial x}\left(\frac{3}{4\pi}\frac{Nx}{V}\right)^{2/3}\frac{h^2}{2m}\right|_{x=\frac{1}{2}} = \frac{4}{3}\epsilon_f\left(\frac{N}{2}\right)$$

so that

$$\begin{aligned}\mu'\left(\frac{N}{2}\right)N &= \left.\frac{\partial}{\partial x}\mu(Nx)\right|_{x=\frac{1}{2}} \\ &\approx \frac{4}{3}\epsilon_f\left(\frac{N}{2}\right)\left(1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_f(\frac{N}{2})}\right)^2\right) \\ &\quad + \frac{8}{3}\epsilon_f\left(\frac{N}{2}\right)\frac{\pi^2}{12}\left(\frac{kT}{\epsilon_f(\frac{N}{2})}\right)^2 \\ &\approx \frac{4}{3}\epsilon_f\left(\frac{N}{2}\right)\left(1 + \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_f(\frac{N}{2})}\right)^2\right)\end{aligned} \tag{14.94}$$

However, the Fermi energy $\epsilon_f(N/2)$ of a Fermi gas with $g = 1$ is just the Fermi energy of the real system with N particles in the case without an external field ($g = 2$), since

$$\epsilon_f\left(\frac{N}{2}\right) = \left(\frac{3}{4\pi}\frac{N}{2V}\right)^{2/3}\frac{h^2}{2m} = \left(\frac{3}{4\pi}\frac{N}{gV}\right)^{2/3}\frac{h^2}{2m} \qquad \text{with} \qquad g = 2$$

Thus, we may identify $\epsilon_f(N/2)$ with the Fermi energy of the whole system in the case without a field. If we insert Equations (14.94) into the expression for the susceptibility (14.92), it follows that

$$\begin{aligned}\chi &\approx \frac{3}{2}\frac{\mu_B^2 N}{\epsilon_f}\left(1 + \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_f}\right)^2\right)^{-1} \\ &\approx \chi_0\left(1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_f}\right)^2\right) \qquad \text{for} \qquad kT \ll \epsilon_f\end{aligned} \tag{14.95}$$

The quantity χ_0 is the susceptibility in the limit $T = 0$,

$$\chi_0 = \frac{3}{2}\frac{\mu_B^2 N}{\epsilon_f} \qquad \text{for} \qquad T = 0 \tag{14.96}$$

The paramagnetic behavior of a Fermi gas of electrons is given by Curie's law for large temperatures or small Fermi energies, respectively (classical limit). For electrons in the conduction

band in metals, however, this is not correct because $kT \ll \epsilon_f$. For these electrons Equations (14.95) or (14.96) are valid; thus the susceptibility of paramagnetic metals depends only very weakly on the temperature. Pauli realized around 1927 that the fact that the susceptibility of paramagnetic alkali metals does not depend on the temperature is due to the degeneracy of the electron gas in these materials.

On the other hand, the classical Curie law holds to good approximation for many paramagnetic nonmetals, if their atoms have a total spin which is half-integral. The Fermi energy of atoms with half-integral spin is, due to their larger mass (at the same particle density), far smaller than that of electrons, and the classical approximation $kT \gg \epsilon_f$ is therefore valid.

Example 14.7: Landau diamagnetism

While paramagnetic behavior is caused by the alignment of permanent magnetic dipoles in field direction, diamagnetic behavior is due to the induction of circular currents in the material, which leads, according to Lenz' rule, to dipole moments opposite to the direction of the field. Thus, paramagnetic materials enforce the external magnetic field and diamagnetic materials weaken it. In the extreme case of an ideal diamagnetic material, the induced circular currents completely compensate the external magnetic field, and the interior of the material is absolutely free of fields. This displacement of the magnetic field out of an ideal diamagnetic material is observed in superconductors and is known as *Meissner–Ochsenfeld effect.*

Here, however, we do not want to consider this special case. Rather, we want to develop a simple model to describe the diamagnetic behavior of metals. To this end, we start once again with the ideal Fermi gas of the metal electrons in the conduction band. We ignore the permanent magnetic dipole moment of the electrons and take into account only the influence of the magnetic field on the electrons. One can solve the Schrödinger equation exactly for an electron moving in a homogeneous magnetic field, but we do not want to do this here. Rather, we want to derive the one-particle energies via a simple plausibility argument.

If we orientate the magnetic field in the z–direction, the electron continues to move freely in this direction (with a corresponding kinetic energy $p_z^2/2m$), since the Lorentz force always acts perpendicular to the magnetic field. On the other hand, in the xy-plane the electron moves (classically) on circular orbits. For circular orbits, the centrifugal force and the Lorentz force just cancel each other (the electron charge is $-e$):

$$\frac{mv^2}{r}\vec{e}_r - \frac{e}{c}\left(\vec{v} \times \vec{B}\right) = 0$$

Scalar multiplication with $\vec{r}$ and use of $\vec{r} \cdot \left(\vec{v} \times \vec{B}\right) = (\vec{r} \times \vec{v}) \cdot \vec{B}$ yields

$$\frac{1}{2}m\vec{v}^2 = \frac{e}{2mc}(\vec{r} \times \vec{p}) \cdot \vec{B} = \frac{eB}{2mc}L_z \qquad \textbf{(14.97)}$$

If we now interpret the classical kinetic energy $\frac{1}{2}m\vec{v}^2$ as the expectation value of the quantum mechanical kinetic energy and take into account that L_z can assume only the discrete values $j_z\hbar$, the mean kinetic energy in the quantum mechanical treatment of the problem is

$$\langle T \rangle = \frac{e\hbar B}{2mc}j_z$$

Quite analogously, the mean potential energy follows from the potential of a particle in a homogeneous magnetic field (electron charge $q = -e$):

$$V = \frac{e}{mc}\vec{A}\cdot\vec{p} + \frac{e^2}{2mc^2}\vec{A}^2 \qquad \text{with} \qquad \vec{A} = -\frac{1}{2}\left(\vec{r}\times\vec{B}\right)$$

If one neglects the quadratic term, which represents only a small relativistic correction, one has

$$\langle V\rangle = -\frac{e}{2mc}\left(\vec{r}\times\vec{B}\right)\cdot\vec{p} = \frac{e}{2mc}(\vec{r}\times\vec{p})\cdot\vec{B} = \frac{eB}{2mc}L_z$$

The mean potential energy is just as large as the mean kinetic energy, and the one-particle energy simply follows as the sum of both. In the exact calculation, however, the zero–point energy also appears. We finally have

$$\epsilon = \epsilon_j + \epsilon_z \qquad \text{with} \qquad \epsilon_j = \frac{e\hbar B}{mc}\left(j+\frac{1}{2}\right), \quad j = 0, 1, 2, \ldots \text{ and } \epsilon_z = \frac{p_z^2}{2m} \tag{14.98}$$

The restriction to positive components, $L_z > 0$, originates from the fact that the direction of rotation of the negatively charged electrons is fixed: as seen from the z–direction it is clockwise. The energy levels (14.98) are degenerate; i.e., there are several states with the same one-particle energy ϵ_j.

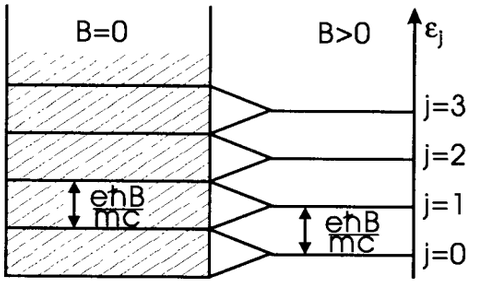


Figure 14.11. Energy levels with and without magnetic field.

One can easily understand this with the help of Figure 14.11. According to this, each discrete level ($j = 0, 1, 2, \ldots$) in the magnetic field results from a superposition of many levels of the nearly continuous spectrum in the case without a magnetic field. Namely, the levels of the field-free case which superpose have an energy $\epsilon = (p_x^2 + p_y^2)/2m$ which lies between the (now discrete) energies $2\mu_B Bj$ and $2\mu_B B(j+1)$.

The number of states g_j which belong to a discrete level j are consequently calculated as

$$g_j = \frac{1}{h^2}\int_{2\mu_B Bj\le\epsilon<2\mu_B B(j+1)} dp_x\, dp_y\, dx\, dy$$

$$\text{with} \quad \epsilon = \frac{1}{2m}\left(p_x^2 + p_y^2\right) \text{ and } \mu_B = \frac{e\hbar}{2mc} \tag{14.99}$$

The integrals over x and y just yield the base area of the container, $V^{2/3}$. The momentum integrals can be solved substituting plane polar coordinates, if we set $p_j = (4m\mu_B Bj)^{1/2}$,

$$g_j = \frac{V^{2/3}}{h^2}2\pi\int_{p_j}^{p_{j+1}} p\,dp = \frac{V^{2/3}}{h^2}\pi\left(p_{j+1}^2 - p_j^2\right) = \frac{V^{2/3}}{h^2}\pi 4m\mu_B B$$

$$g_j = V^{2/3}\frac{eB}{hc} \tag{14.100}$$

The degeneracy factor g_j is independent of j. It vanishes for $B \to 0$, which is not surprising, since we have assumed the limiting case of a continuous spectrum in Equation (14.99).

A remark is in order: One could argue that the degeneracy (14.100) of the jth state contradicts the Pauli principle, since fermions can occupy the angular momentum state j, only

if they differ in other quantum numbers, and this is only a small number, which can by no means be proportional to $V^{2/3}$. However, we have to note that B induces many microscopic, spatially strictly separated current circles. For each current the argument with the Pauli principle may hold, but all in all, each single current circle with an electron with angular momentum projection j in the z–direction contributes to the degeneracy factor g_j. The Pauli principle is not violated, since each current circle is strongly spatially restricted and can be localized (formerly, an electron could not be localized more precisely than being in the spatial region V, i.e., the total volume of the metal). Thus, many electrons may have the same angular momentum projection j, as long as they are in spatially separated current circles.

It seems hopeless to calculate the number of current circles. However, we may exploit the fact that the number of electrons in the metal is constant, and consequently, that electrons which were formerly found in the occupied states $\{p_x, p_y, p_z\}$ in the total volume V are now to be found somewhere in the spatially localized current circles with an angular momentum projection j in z–direction. In Equation (14.97) we have matched the kinetic energy with the angular momentum energy, and the number of respective current circles was (indirectly) calculated with g_j in Equation (14.100).

After these preliminary remarks we are now able to explicitly denote the sum over all states in the logarithm of the grand partition function. We have to integrate over all momenta p_z and to sum over all values of j, where $V^{1/3}\,dp_z/h$ p_z–eigenstates lie in the momentum interval dp_z,

$$\ln \mathcal{Z} = \frac{V^{1/3}}{h} \int_{-\infty}^{+\infty} dp_z \sum_{j=0}^{\infty} g_j \ln \left[1 + z \exp \left\{ -\beta \left(\frac{p_z^2}{2m} + 2\mu_B B \left(j + \frac{1}{2} \right) \right) \right\} \right] \tag{14.101}$$

The chemical potential can be determined for fixed (mean) particle number from

$$N = \frac{V^{1/3}}{h} \int_{-\infty}^{+\infty} dp_z \sum_{j=0}^{\infty} g_j \frac{1}{z^{-1} \exp \left\{ \beta \left(\frac{p_z^2}{2m} + 2\mu_B B \left(j + \frac{1}{2} \right) \right) \right\} + 1} \tag{14.102}$$

Unfortunately, the evaluation of Equations (14.101) and (14.102) is nontrivial. Thus, we first want to restrict ourselves to the most simple limiting cases.

To this end, we consider the orders of magnitude of the characteristic energies ϵ_f, kT, and $\mu_B B$ of the system. The Fermi energy ϵ_f of the electron gas in metals is of the order of a few electron volts. The mean thermal energy kT at room temperature is approximately $\frac{1}{40}$ eV, and the energy of the induced dipole is still very small for a magnetic field of 1 T, $\mu_B B \approx 10^{-4}$ eV. We may therefore assume $\epsilon_f \gg kT \gg \mu_B B$. The energy levels ϵ_j are very dense for small field strengths, and one can therefore approximately calculate the sum over j in Equation (14.101) with the Euler–MacLaurin formula:

$$\sum_{j=0}^{\infty} f\left(j + \frac{1}{2} \right) \approx \int_0^{\infty} f(x)\,dx + \frac{1}{24} f'(0) + \cdots \tag{14.103}$$

With $f(x) = \ln \left[1 + z \exp \left\{ -\beta \left(\frac{p_z^2}{2m} + 2\mu_B B x \right) \right\} \right]$ one obtains for Equation (14.101)

$$\ln \mathcal{Z} \approx \frac{VeB}{h^2 c} \left(\int_0^{\infty} dx \int_{-\infty}^{+\infty} dp_z \ln \left[1 + z \exp \left\{ -2\beta \mu_B B x - \frac{\beta p_z^2}{2m} \right\} \right] \right.$$

$$- \frac{1}{12}\beta\mu_B B \int_{-\infty}^{+\infty} dp_z \frac{1}{z^{-1}\exp\left\{\frac{\beta p_z^2}{2m}\right\}+1}\Bigg) \tag{14.104}$$

Instead of $\int_{-\infty}^{+\infty} dp_z$ one may also write $2\int_0^{\infty} dp_z$, since only p_z^2 enters the integrand. In the next step we substitute the new variable $\epsilon = 2\mu_B Bx + p_z^2/2m$ in the first integrand. Instead of integrating over x we integrate over ϵ from 0 to ∞. We first perform the integration over p_z for *fixed* ϵ. For fixed ϵ the minimum of p_z is just zero (if $x = \epsilon/2\mu_B B$) and the maximum is $\sqrt{2m\epsilon}$ (if $x = 0$). By the way, one can convince oneself with the help of a small illustrative figure of the p_z–x–plane that the integration over ϵ and p_z (instead of over x and p_z) with the prescription just mentioned covers the same integration region and that the substitution is regular. If we denote the first term in Equation (14.104) as $\ln \mathcal{Z}_0$, it follows that

$$\begin{aligned}\ln \mathcal{Z}_0 &= \frac{VeB}{h^2 c}\frac{1}{\mu_B B}\int_0^{\infty} d\epsilon \int_0^{\sqrt{2m\epsilon}} dp_z \ln\left[1 + z\exp\{-\beta\epsilon\}\right] \\ &= \frac{2\pi V(2m)^{3/2}}{h^3}\int_0^{\infty} d\epsilon\epsilon^{1/2}\ln\left[1 + z\exp\{-\beta\epsilon\}\right]\end{aligned}$$

This is just the partition function of a free Fermi gas without a magnetic field. As one observes, the first term in Equation (14.103) reproduces the limiting case $B \to 0$. The higher order terms thus represent corrections to the free case. If we denote the second term in Equation (14.104) by $\ln \mathcal{Z}_1$ and substitute $y = \beta p_z^2/2m$, the integral becomes

$$\begin{aligned}\ln \mathcal{Z}_1 &= -\frac{\pi V(2m)^{3/2}}{6h^3}(\mu_B B)^2\beta^{1/2}\int_0^{\infty}\frac{y^{-1/2}\,dy}{z^{-1}e^y + 1} \\ &= -\frac{\pi V(2m)^{3/2}}{6h^3}(\mu_B B)^2\beta^{1/2}\sqrt{\pi}\,f_{1/2}(z)\end{aligned}$$

Because $z \gg 1$ ($\epsilon_f \gg kT$), the function $f_{1/2}(z) \approx (\ln z)^{1/2}/\Gamma(3/2) \approx 2/\sqrt{\pi}$ $(\epsilon_f/kT)^{1/2}$ may be approximated (cf. Equation (14.26)). Moreover, the prefactors can be written more clearly in terms of the Fermi energy (14.44):

$$\ln \mathcal{Z}_1 \approx -\frac{N}{4}\frac{(\mu_B B)^2}{\epsilon_f kT}$$

Here $g = 1$, since the spin degeneracy is removed due to the magnetic field. From $\ln \mathcal{Z}_1$ one readily derives the mean magnetic moment, since $\ln \mathcal{Z}_0$ does not depend on B,

$$\langle D_z\rangle = \frac{1}{\beta}\frac{\partial}{\partial B}\ln \mathcal{Z}_1\Big|_{z,V,T} = -\frac{1}{2}N\mu_B\left(\frac{\mu_B B}{\epsilon_f}\right) \qquad \text{for} \qquad \epsilon_f \gg kT \gg \mu_B B \tag{14.105}$$

Finally, the susceptibility becomes

$$\chi_0 = \lim_{B\to 0}\frac{\partial\langle D_z\rangle}{\partial B} = -\frac{1}{2}\frac{N\mu_B^2}{\epsilon_f}$$

Quite similar results were obtained in the paramagnetic case (Example 14.6), with an additional factor 3 and the opposite sign. The latter results, of course, from the mean magnetic moment (14.105) oriented opposite to the field direction, which is typical for induced dipoles. The diamagnetic susceptibility of the electron gas is temperature independent for $kT \ll \epsilon_f$, as is the corresponding paramagnetic susceptibility. In metals, paramagnetic and diamagnetic

moments will superpose, so that an effective susceptibility

$$\chi_0^{\text{eff}} = \chi_0^{\text{dia}} + \chi_0^{\text{para}} = \frac{1}{2}\frac{N}{\epsilon_f}\left(3\mu_B^2 - \mu_B'^2\right) \tag{14.106}$$

remains, which corresponds to paramagnetic behavior. Here we have written $\mu_B' = e\hbar/(2m'c)$ for the diamagnetic part. The metal electrons can approximately move freely, but due to the residual interactions (mutually and with the ions) they have an effective mass m', which is more or less distinct from the free mass m. Since the diamagnetic moment originates from the induced circular motion of the electrons with this effective mass, the magneton, which is to be inserted into Equation (14.106) may differ from the usual value μ_B. In the paramagnetic part, however, this consideration does not hold, since here the magnetic moment is due to the spin, the absolute value of which does not change due to interactions.

We now want to calculate the Boltzmann limit $kT \gg \epsilon_f$ of Equation (14.101), at first for an arbitrary magnetic field. In this case $z \ll 1$, and one may insert Boltzmann statistics in Equation (14.101) ($\ln(1 + \alpha z) \approx \alpha z$):

$$\ln \mathcal{Z} = \frac{zVeB}{h^2c}\int_{-\infty}^{+\infty} dp_z \exp\left\{-\beta\frac{p_z^2}{2m}\right\}\sum_{j=0}^{\infty}\exp\left\{-\beta 2\mu_B B\left(j + \frac{1}{2}\right)\right\}$$

The momentum integral is meanwhile well known, and we have already met the sum over j in a different context (Example 8.1):

$$\ln \mathcal{Z} = \frac{zVeB}{h^2c}\left(\frac{2\pi m}{\beta}\right)^{1/2}[2\sinh(\beta\mu_B B)]^{-1} \qquad \text{for} \qquad kT \gg \epsilon_f \tag{14.107}$$

Here the chemical potential has to be determined from Equation (14.102) in the Boltzmann limit $z \ll 1$. Instead of performing this calculation it is simpler to differentiate $\ln \mathcal{Z}$:

$$N = z\left.\frac{\partial}{\partial z}\ln \mathcal{Z}\right|_{B,V,T} = \frac{zV}{\lambda^3}\frac{x}{\sinh x} \qquad \text{with} \qquad x = \beta\mu_B B \tag{14.108}$$

from which z is readily calculated. For high temperatures, $T \to \infty$, $x \approx 0$ and $(\sinh x)/x \approx 1$. The chemical potential (or the fugacity z) then approximates the classical ideal gas value $z \approx n\lambda^3$.

The mean magnetic moment is given by

$$\langle D_z\rangle = \frac{1}{\beta}\left.\frac{\partial}{\partial B}\ln \mathcal{Z}\right|_{z,V,T} = \frac{zV}{\lambda^3}\mu_B\frac{x}{\sinh x}\left\{\frac{1}{x} - \coth x\right\} \qquad \text{for} \qquad kT \gg \epsilon_f$$

If one inserts Equation (14.108) and uses the definition of the Langevin Function (cf. Chapter 8), one has

$$\langle D_z\rangle = -N\mu_B L(x) \tag{14.109}$$

This expression has—up to the sign—the same form as in the Boltzmann limit of the paramagnetic case, Chapter 8. Again, the minus sign in Equation (14.109) can be traced to the orientation of the induced dipoles opposite to the field. However, note that here we obtain in the limit a dipole with arbitrary orientation. In the preceding Example the Boltzmann limit yielded the case of quantum mechanical dipoles with $j = \frac{1}{2}$ and only two orientations (cf. Example 14.6, Chapter 8). The reason is that the paramagnetic moments of the free electrons are due to the spin, which has the fixed value $j = \frac{1}{2}$. On the other hand, the diamagnetic moment of an electron in a circular orbit does not depend on the total angular momentum of

the electron, but only on the z–component j_z. However, arbitrarily large angular momenta also contribute to a given component j_z.

Example 14.8: De Haas–van Alphen effect

Up to now we have evaluated Equation (14.101) only in the cases $\epsilon_f \gg kT \gg \mu_B B$ and $kT \gg \epsilon_f$. The first case is quite realistic at room temperature, since the Fermi energy of metal electrons is large compared to the thermal energy kT. However, $kT \gg \mu_B B$ was also a necessary condition, since only then the discrete levels ϵ_j are sufficiently dense so that the Euler–MacLaurin formula can be terminated after the second term.

We now want to study the case of very small temperatures and comparatively strong magnetic fields $kT \approx \mu_B B \ll \epsilon_f$. We will show that just then an interesting new effect appears, which is connected with the degeneracy of the electron gas. In this case, oscillatory terms in the characteristic variable $\epsilon_f/\mu_B B$ enter the grand canonical potential. It would be very complicated to try to sum up the Euler–MacLaurin series in Equation (14.103) completely. Therefore we pursue another path. First, we once again denote the general prescription to calculate $\ln \mathcal{Z}$:

$$\ln \mathcal{Z} = \sum_k \ln\left(1 + z\exp\{-\beta\epsilon_k\}\right) = \int_0^\infty d\epsilon g_1(\epsilon) \ln\left(1 + z\exp\{-\beta\epsilon\}\right) \qquad \textbf{(14.110)}$$

In the formulation for continuous one-particle energies the one-particle state density $g_1(\epsilon)$ appears. We now want to determine it explicitly. To this end we use the results of Chapter 7, according to which $g_1(\epsilon)$ follows from the Laplace transformation of the canonical partition function in the Boltzmann limit,

$$g_1(\epsilon) = \frac{1}{2\pi i} \int_{\beta'-i\infty}^{\beta'+i\infty} \exp\{\beta\epsilon\} Z_1^B(\beta)\, d\beta, \qquad \beta' > 0 \qquad \textbf{(14.111)}$$

We can easily write down the canonical partition function $Z_1^B(\beta)$, since we have already calculated the corresponding grand partition function in Equation (14.107). In general, it holds for noninteracting system that

$$\ln \mathcal{Z} = z Z_1^B(\beta)$$

With Equation (14.107), we have for $\ln \mathcal{Z}$

$$Z_1^B(\beta) = \frac{VeB}{h^2 c} \left(\frac{2\pi m}{\beta}\right)^{1/2} [2\sinh(\alpha\beta)]^{-1} \qquad \text{with} \qquad \alpha = \mu_B B \qquad \textbf{(14.112)}$$

Note that the calculation of $g_1(\epsilon)$ via $Z_1^B(\beta)$ in the Boltzmann limit ($kT \gg \epsilon_f$) has nothing to do with the real temperatures, which on the contrary fulfill $kT \ll \epsilon_f$. We just have to get $g_1(\epsilon)$ somehow, which we need in Equation (14.110) for the evaluation of the (quantum statistically correct) grand partition function. One way to calculate $g_1(\epsilon)$ is by definition over the canonical partition function in the Boltzmann limit according to Equation (14.111). Now the complex contour integral (14.111) has to be calculated using Equation (14.112),

$$g_1(\epsilon) = \frac{VeB}{2h^2 c} (2\pi m)^{1/2} \frac{1}{2\pi i} \int_{\beta'-i\infty}^{\beta'+i\infty} \frac{\exp\{\beta\epsilon\} d\beta}{\beta^{1/2}\sinh(\alpha\beta)}$$

The calculation of this integral is performed in the next Exercise. The result is

$$g_1(\epsilon) = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \left[\epsilon^{1/2} + \alpha^{1/2} \sum_{l=1}^{\infty} \frac{(-1)^l}{l^{1/2}} \cos\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)\right]$$

or, if the prefactors are expressed in terms of the Fermi energy ϵ_f of the electron gas with degeneracy $g = 1$ (no spin degeneracy),

$$g_1(\epsilon) = \frac{3}{2} N \epsilon_f^{-3/2} \left[\epsilon^{1/2} + \alpha^{1/2} \sum_{l=1}^{\infty} \frac{(-1)^l}{l^{1/2}} \cos\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)\right]$$

One immediately recognizes that the first term in brackets yields the state density of the ideal Fermi gas in the absence of a magnetic field. Thus, this part leads to the grand canonical potential of the ideal Fermi gas only in the case $\beta \to 0$ ($\alpha \to 0$), and we abbreviate

$$\ln \mathcal{Z} = \ln \mathcal{Z}_0 + \ln \mathcal{Z}_B$$

where $\ln \mathcal{Z}_0$ was already extensively studied for the ideal Fermi gas and is here of no further interest. The second part carries the index B to illustrate the influence of the magnetic field, and reads

$$\ln \mathcal{Z}_B = \int_0^{\infty} g_B(\epsilon)\, d\epsilon \ln\left(1 + z \exp\{-\beta\epsilon\}\right) \qquad \textbf{(14.113)}$$

with

$$g_B(\epsilon) = \frac{3}{2} \frac{N}{\epsilon_f} \left(\frac{\alpha}{\epsilon_f}\right)^{1/2} \sum_{l=1}^{\infty} \frac{(-1)^l}{l^{1/2}} \cos\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)$$

This part of the state density describes the conglomeration of the states according to Figure 14.11. The function $g_B(\epsilon)$ is periodic in the variable $x = \epsilon/\alpha$, with the period $\Delta x = 2$. In particular, $g_B(\epsilon)$ diverges at $x = 1, 3, 5, \ldots$. For $x = (2n + 1), n = 0, 1, 2, \ldots$ we namely have

$$\cos\left(l\pi(2n + 1) - \frac{\pi}{4}\right) = \cos\left(l\pi - \frac{\pi}{4}\right) = \frac{1}{\sqrt{2}}(-1)^l$$

and $g_B(\epsilon)$ becomes proportional to

$$\sum_{l=1}^{\infty} \frac{1}{l^{1/2}} \to \infty$$

The points $x = 2n + 1$ correspond to the discrete states ϵ_j, because $\epsilon = (2n + 1)\alpha = 2\mu_B B\left(n + \frac{1}{2}\right)$. Only the logarithm under the integral is disturbing in the further evaluation of Equation (14.113). On the other hand, we know that the derivative of this term with respect to the energy is just proportional to the mean occupation number $\langle n_\epsilon \rangle^{\mathrm{FD}}$. Especially for low temperatures, this quantity has the form of a Θ–function ($\Theta(\epsilon_f - \epsilon)$). Therefore, the derivative of the occupation number shows a sharp maximum at the Fermi energy in the case of interest. It is thus convenient to integrate by parts (twice) in Equation (14.113):

$$\begin{aligned}
\ln \mathcal{Z}_B &= \left[G(\epsilon) \ln(1 + z \exp\{-\beta\epsilon\})\right]_0^{\infty} + \beta \int_0^{\infty} d\epsilon G(\epsilon) \frac{1}{z^{-1} \exp\{\beta\epsilon\} + 1} \\
&= \left[G(\epsilon) \ln(1 + z \exp\{-\beta\epsilon\})\right]_0^{\infty} + \left[\frac{\beta \mathcal{G}(\epsilon)}{z^{-1} \exp\{\beta\epsilon\} + 1}\right]_0^{\infty}
\end{aligned}$$

$$-\beta \int_0^\infty d\epsilon \mathcal{G}(\epsilon) \frac{\partial}{\partial \epsilon} \frac{1}{z^{-1} \exp\{\beta\epsilon\} + 1} \tag{14.114}$$

The functions $G(\epsilon)$ and $\mathcal{G}(\epsilon)$ of $g_B(\epsilon)$ can be readily denoted:

$$G(\epsilon) = \frac{3}{2\pi} N \left(\frac{\alpha}{\epsilon_f}\right)^{3/2} \sum_{l=1}^{\infty} \frac{(-1)^l}{l^{3/2}} \sin\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right) \tag{14.115}$$

$$\mathcal{G}(\epsilon) = -\frac{3}{2\pi^2} N\alpha \left(\frac{\alpha}{\epsilon_f}\right)^{3/2} \sum_{l=1}^{\infty} \frac{(-1)^l}{l^{5/2}} \cos\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right) \tag{14.116}$$

The advantage of this calculation is that the integrand in the last integral in Equation (14.114) contributes practically only in the vicinity of the Fermi energy.

First, we consider the terms integrated by parts. These have to vanish at the upper boundary, since $G(\epsilon)$ as well as $\mathcal{G}(\epsilon)$ are bounded periodic functions and $\exp\{-\beta\epsilon\} \to 0$ for $\epsilon \to \infty$. At the lower boundary these terms yield the contributions $G(0)\ln(1+z)$ and $\beta\mathcal{G}(0)(z^{-1}+1)^{-1}$, which do not vanish. Of course, these terms can be calculated using Equations (14.115) and (14.116) and $z \approx \exp\{\epsilon_f/kT\} \gg 1$. They yield a contribution which depends on B and N, but is not of oscillatory nature in B. We now want to study the oscillatory terms. The oscillating part of the partition function reads

$$\ln \mathcal{Z}_{\text{osc}} \approx -\beta \int_0^\infty \mathcal{G}(\epsilon)\, d\epsilon \frac{\partial}{\partial \epsilon} \frac{1}{z^{-1} \exp\{\beta\epsilon\} + 1} \tag{14.117}$$

Now, we have

$$\frac{\partial}{\partial \epsilon} \frac{1}{z^{-1} \exp\{\beta\epsilon\} + 1} = -\beta \frac{z^{-1} \exp\{\beta\epsilon\}}{(z^{-1} \exp\{\beta\epsilon\} + 1)^2} = -\frac{\beta}{4} \cosh^{-2}\left(\frac{\beta}{2}(\epsilon - \mu)\right) \tag{14.118}$$

where we may set $\mu \approx \epsilon_f$ because $kT \ll \epsilon_f$. If we insert Equations (14.118) and (14.116) into Equation (14.117), we have to calculate

$$\ln \mathcal{Z}_{\text{osc}} \approx -\frac{3}{8\pi^2} N\alpha\beta^2 \left(\frac{\alpha}{\epsilon_f}\right)^{3/2} \sum_{l=1}^{\infty} \frac{(-1)^l}{l^{5/2}} \int_0^\infty d\epsilon \frac{\cos\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)}{\cosh^2\left(\frac{\beta}{2}(\epsilon - \epsilon_f)\right)}$$

The integral has the value

$$\int_0^\infty d\epsilon \frac{\cos\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)}{\cosh^2\left(\frac{\beta}{2}(\epsilon - \epsilon_f)\right)} \approx \frac{4}{\beta} \cos\left(\frac{l\pi\epsilon_f}{\alpha} - \frac{\pi}{4}\right) \frac{\frac{l\pi^2}{\alpha\beta}}{\sinh\left(\frac{l\pi^2}{\alpha\beta}\right)} \tag{14.119}$$

(see Exercise 14.10). The result is intuitively clear, since the denominator in the integrand produces a sharp maximum at ϵ_f for $\beta \to \infty$, and in the limit even a δ–function. Thus, one obtains the numerator at ϵ_f, multiplied by correction factors for finite temperatures. The final result reads

$$\ln \mathcal{Z}_{\text{osc}} \approx -\frac{3}{2} N \left(\frac{\alpha}{\epsilon_f}\right)^{3/2} \sum_{l=1}^{\infty} \frac{(-1)^l}{l^{3/2}} \frac{\cos\left(\frac{l\pi\epsilon_f}{\alpha} - \frac{\pi}{4}\right)}{\sinh\left(\frac{l\pi^2}{\alpha\beta}\right)} \tag{14.120}$$

As one observes, the grand canonical potential indeed contains oscillatory terms in the variable $\epsilon_f/\mu_B B$. For high temperatures ($kT \gg \mu_B B$), however, these terms are barely perceptible, since then the hyperbolic sine in the denominator becomes very large and dampens everything

away. On the other hand, if kT is of the order of $\mu_B B$, then $\alpha\beta \approx 1$. Then only the term $l = 1$ in Equation (14.120) contributes noticeably, since for the other terms the sinh again grows exponentially. If one restricts oneself to this term, one obtains an oscillating contribution to the magnetic moment,

$$\begin{aligned}\langle D_z\rangle_{\text{osc}} &= \frac{1}{\beta}\frac{\partial}{\partial B}\ln Z_{\text{osc}} \\ &= \frac{3}{2}\frac{N\mu_B}{\beta\epsilon_f^{3/2}}\frac{\partial}{\partial\alpha}\left[\alpha^{3/2}\frac{\cos\left(\frac{\pi\epsilon_f}{\alpha}-\frac{\pi}{4}\right)}{\sinh\left(\frac{\pi^2}{\alpha\beta}\right)}\right] \\ &\approx \frac{3\pi}{2}\frac{N\mu_B}{\epsilon_f}\frac{1}{\beta}\left(\frac{\epsilon_f}{\alpha}\right)^{1/2}\frac{\sin\left(\frac{\pi\epsilon_f}{\alpha}-\frac{\pi}{4}\right)}{\sinh\left(\frac{\pi^2}{\alpha\beta}\right)}+\cdots\end{aligned}$$

where we have retained only the leading order term (namely the term proportional to ϵ_f, since $\epsilon_f \gg \alpha$). We calculate the corresponding susceptibility according to $\chi = \langle D_z\rangle / B$, since the limit $B \to 0$ is not sensible for the strong fields considered here:

$$\chi_{\text{osc}} \approx \frac{3\pi}{2}\frac{N\mu_B^2}{\epsilon_f}\frac{kT\epsilon_f^{1/2}}{(\mu_B B)^{3/2}}\frac{\sin\left(\frac{\pi\epsilon_f}{\mu_B B}-\frac{\pi}{4}\right)}{\sinh\left(\frac{\pi^2 kT}{\mu_B B}\right)} \qquad \text{for} \qquad \mu_B B \approx kT \ll \epsilon_f \tag{14.121}$$

This expression can be directly compared to the smooth diamagnetic or paramagnetic contributions. Also, the susceptibility has, according to Equation (14.121), an oscillatory contribution in the variable $\epsilon_f/\mu_B B$ for strong magnetic fields and low temperatures. If one measures the susceptibility of a metal as a function of the field strength B at very low temperatures, one can directly determine the Fermi energy of the metal from the periodic variations. However, the measurement is not simple, since, as already mentioned, the magnetic fields have to be very strong and the temperature very low. Even then, the smooth diamagnetic and paramagnetic contributions to the susceptibility are rather large in comparison to the actual effect.

The reason for the oscillations is, of course, the conglomeration of the states in the region of the quantized circular orbits. At very low temperatures, without a magnetic field, the Fermi occupation of the states is nearly rectangular, and only a few electrons in a region kT around the Fermi energy are excited. If the field strength is now increased, the discrete levels ϵ_j are formed with the degeneracy (high state density) g_j discussed in the last Example. If B is further enlarged, the difference between the energy levels increases and the degeneracy grows, since more continuous momentum states have to fit into each angular momentum level. If such a congestion happens to be near the Fermi edge, relatively more electrons can be excited, and this changes the susceptibility. As B is continuously increased congestions pass the Fermi edge, one after another, and thus lead to the periodic variations of χ. For weak fields, however, the congestions are close to each other and have a small degeneracy. Thus, the effect vanishes for $\mu_B B \ll kT \ll \epsilon_f$. The same happens for higher temperature, since then the energy range kT around the Fermi edge, where electrons are excited, becomes larger than the distance between the congestions.

The periodic behavior of the susceptibility of metals at low temperatures and strong magnetic fields is known as *de Haas–van Alphen effect.*

Exercise 14.9: Calculation of the state density of Landau diamagnetism

Calculate the state density

$$g_1(\epsilon) = \frac{VeB}{2h^2c}(2\pi m)^{1/2}\frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty}\frac{\exp\{\beta\epsilon\}\,d\beta}{\beta^{1/2}\sinh(\alpha\beta)} \tag{14.122}$$

Solution The integrand has poles at $\beta = 0$ and where the sinh vanishes. This is the case along the imaginary β–axis for $\alpha\beta = il\pi$, with $l = 0, \pm1, \pm2, \ldots$. As in Example 7.11 the integration contour can be closed in the complex β–plane. For $\epsilon > 0$ this must be done via path 2 (see Figure 14.12), since here the denominator vanishes for $|\beta| \to \infty$. For $|\beta| \to \infty$ and $\epsilon > 0$ the half circle 2 does not contribute to the contour integral at infinity. Analogously, for $\epsilon < 0$ path 1 has to be chosen. Since no poles are inside the contour for path 1, the contour integral and consequently the state density vanish for $\epsilon < 0$.

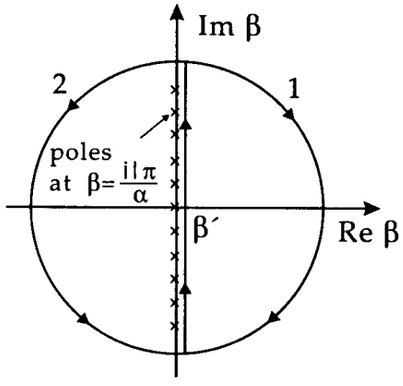


Figure 14.12. Integration contour in the complex β–plane.

For $\epsilon > 0$, however, the poles on the imaginary axis are enclosed, and Equation (14.122) has to be calculated according to the residue theorem.

According to the rules for complex contour integrals, path 1 is equivalent to the sum of the contours shown in Figure 14.13, where we integrate along a small circle around the poles $\beta = il\pi/\alpha$. This is of course nothing but the prescription for calculating residues.

We first consider the pole at $\beta = 0$. If we integrate along a small circle around $\beta = 0$, we may set $\sinh(\alpha\beta) \approx \alpha\beta$, and the contribution of this pole to the total integral becomes

$$\frac{1}{2\pi i}\oint_{\beta=0}\frac{\exp\{\beta\epsilon\}\,d\beta}{\beta^{1/2}\sinh(\alpha\beta)} = \frac{1}{2\pi i\alpha}\oint\frac{\exp\{\beta\epsilon\}}{\beta^{3/2}}d\beta = \frac{1}{\alpha}\frac{\epsilon^{1/2}}{\Gamma\left(\frac{3}{2}\right)}$$

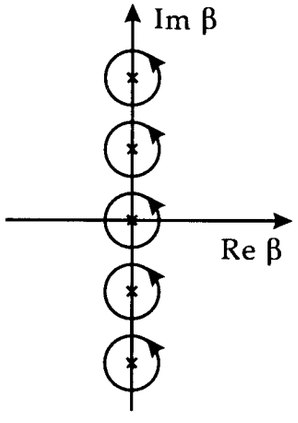


Figure 14.13. Integration contours around the poles.

where we have used results from Example 7.11.

To calculate the residues of the remaining poles we use the general formula

$$\frac{1}{2\pi i}\oint_{z_0}\frac{f(z)}{z-z_0}dz = f(z_0)\frac{1}{2\pi i}\oint_{z_0}\frac{dz}{z-z_0} = f(z_0) \tag{14.123}$$

if $f(z)$ is holomorphic in z_0 and the contour around z_0 is positively oriented and simply closed. Since the circles around the poles may become arbitrarily small, the sinh in the denominator can be expanded around the respective pole:

$$\begin{aligned}\sinh(\alpha\beta) &\approx \sinh(il\pi) + \cosh(il\pi)(\alpha\beta - il\pi) + \cdots \\ &\approx (-1)^l(\alpha\beta - il\pi) + \cdots\end{aligned} \tag{14.124}$$

The integrals can be immediately evaluated using Equations (14.123) and (14.124):

$$\begin{aligned}&\frac{1}{2\pi i}\oint_{\beta=\frac{il\pi}{\alpha}}\frac{\exp\{\beta\epsilon\}\,d\beta}{\beta^{1/2}\sinh(\alpha\beta)} \\ &= \left(\frac{il\pi}{\alpha}\right)^{-1/2}\exp\left\{i\frac{l\pi\epsilon}{\alpha}\right\}\frac{(-1)^l}{\alpha}\frac{1}{2\pi i}\oint\frac{d\beta}{\beta - \frac{il\pi}{\alpha}}\end{aligned}$$

$$= \left(\frac{il\pi}{\alpha}\right)^{-1/2} \exp\left\{i\,\frac{l\pi\epsilon}{\alpha}\right\}\,\frac{(-1)^l}{\alpha}$$

The integral in Equation (14.122) has therefore the value

$$\frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty}\frac{\exp\{\beta\epsilon\}\,d\beta}{\beta^{1/2}\sinh(\alpha\beta)}$$

$$= \frac{1}{\alpha}\left[\frac{2}{\sqrt{\pi}}\epsilon^{1/2} + \sum_{l=-\infty,l\neq 0}^{\infty}(-1)^l\left(\frac{il\pi}{\alpha}\right)^{-1/2}\exp\left\{i\,\frac{l\pi\epsilon}{\alpha}\right\}\right]$$

Here one can summarize the terms for $\pm l$, because

$$\frac{1}{i^{1/2}}\exp\left\{i\,\frac{l\pi\epsilon}{\alpha}\right\} + \frac{1}{(-i)^{1/2}}\exp\left\{-i\,\frac{l\pi\epsilon}{\alpha}\right\}$$

$$= \exp\left\{i\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)\right\} + \exp\left\{-i\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)\right\}$$

$$= 2\cos\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)$$

The one-particle state density thus reads

$$g_1(\epsilon) = \frac{VeB}{2h^2c}(2\pi m)^{1/2}\frac{1}{\alpha}\left[\frac{2}{\sqrt{\pi}}\epsilon^{1/2} + 2\left(\frac{\alpha}{\pi}\right)^{1/2}\sum_{l=1}^{\infty}\frac{(-1)^l}{l^{1/2}}\cos\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)\right]$$

With $\alpha = \mu_B B$ this can be written in simpler terms:

$$g_1(\epsilon) = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\left[\epsilon^{1/2} + \alpha^{1/2}\sum_{l=1}^{\infty}\frac{(-1)^l}{l^{1/2}}\cos\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)\right]$$

Exercise 14.10: Calculation of integral (14.119) of Example 14.8

Calculate the integral

$$I = \int_0^{\infty} d\epsilon\,\frac{\cos\left(\frac{l\pi\epsilon}{\alpha} - \frac{\pi}{4}\right)}{\cosh^2\left(\frac{\beta}{2}(\epsilon - \epsilon_f)\right)}$$

Solution One substitutes the new variable $x = \frac{\beta}{2}(\epsilon - \epsilon_f)$:

$$I = \frac{2}{\beta}\int_{-\frac{\beta}{2}\epsilon_f}^{\infty}\frac{\cos\left(\frac{2l\pi}{\alpha\beta}x + l\pi\frac{\epsilon_f}{\alpha} - \frac{\pi}{4}\right)}{\cosh^2 x}\,dx$$

For low temperatures $kT \ll \epsilon_f$ we have $\beta\epsilon_f/2 \gg 1$, and one may replace the lower boundary of the integral by $-\infty$. The error introduced by this is exponentially small, since $\cosh^{-2} x$ vanishes exponentially for $x \to \pm\infty$. Furthermore, the numerator can be decomposed with the help of the addition theorems for the trigonometric functions,

$$I = \frac{2}{\beta}\left[\cos\left(\frac{l\pi}{\alpha}\epsilon_f - \frac{\pi}{4}\right)\int_{-\infty}^{+\infty}dx\,\frac{\cos\left(\frac{2l\pi}{\alpha\beta}x\right)}{\cosh^2 x}\right.$$

$$- \sin\left(\frac{l\pi}{\alpha}\epsilon_f - \frac{\pi}{4}\right)\int_{-\infty}^{+\infty} dx\,\frac{\sin\left(\frac{2l\pi}{\alpha\beta}x\right)}{\cosh^2 x}\Bigg]$$

The second integral just vanishes, since the integrand is odd. With the abbreviation $\gamma = \frac{2l\pi}{\alpha\beta}$ we only have to calculate

$$\int_{-\infty}^{+\infty} dx\,\frac{\cos\gamma x}{\cosh^2 x} = \int_{-\infty}^{+\infty} dx\,\frac{\exp\{i\gamma x\}}{\cosh^2 x} \tag{14.126}$$

In the second step a corresponding integral with a sine in the numerator was added, which is zero (integrand is odd).

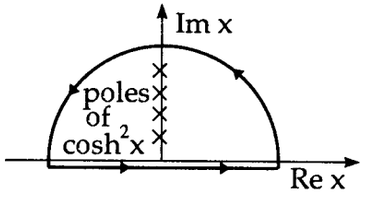


Figure 14.14. Integration contour in the complex x–plane.

However, the integral in Equation (14.126) can again be completed as a closed contour integral in the complex x–plane (see Figure 14.14). The contour is closed in the half plane $\Im x > 0$ from $+\infty$ to $-\infty$, since for $\gamma > 0$ the numerator vanishes exponentially for $\Im x \to \infty$, while the numerator converges to zero at most quadratically (for $\Re x = 0$ and $\Im x = \frac{\pi}{2} \bmod \pi$). Thus, the contribution of the half circle to the integral vanishes. The value of this integral is again just given by the sum of the residues of the integrand (the poles of $\cosh^{-2} x$).

These are $x_n = i\pi(n + \frac{1}{2})$ with $n = 0, 1, 2, \ldots$. As in the preceding Exercise, we sum the integrals along small circles around the poles,

$$\int_{-\infty}^{+\infty} dx\,\frac{\cos\gamma x}{\cosh^2 x} = \sum_{n=0}^{\infty}\oint_{i\pi(n+\frac{1}{2})}\frac{\exp\{i\gamma x\}}{\cosh^2 x}\,dx$$

We now substitute the new complex variable $y = x - i\pi(n + \frac{1}{2})$, and obtain with $\cosh^2(y + i\pi(n + \frac{1}{2})) = -\sinh^2 y$,

$$\int_{-\infty}^{+\infty} dx\,\frac{\cos\gamma x}{\cosh^2 x} = -\sum_{n=0}^{\infty}\exp\left\{-\gamma\pi\left(n + \frac{1}{2}\right)\right\}\oint_{y=0}\frac{\exp\{i\gamma y\}}{\sinh^2 y}\,dy \tag{14.127}$$

In the last integral one integrates only around the pole at $y = 0$. To determine the residue one expands the integrand in terms of a Laurent series around $y = 0$. As one knows, the residue is simply the coefficient a_{-1} of y^{-1}, and the integral has the value $2\pi i a_{-1}$. We have

$$\frac{\exp\{i\gamma y\}}{\sinh^2 y} = \frac{(1 + i\gamma y + \cdots)}{\left(y + \frac{y^2}{6} + \cdots\right)^2}$$

$$= \frac{(1 + i\gamma y + \cdots)}{y^2}\left(1 - \frac{y^2}{3} + \cdots\right) = \frac{1}{y^2} + i\gamma\frac{1}{y} + \cdots$$

thus $a_{-1} = i\gamma$. With this result we find for Equation (14.126)

$$\int_{-\infty}^{+\infty} dx\,\frac{\cos\gamma x}{\cosh^2 x} = 2\pi\gamma\sum_{n=0}^{\infty}\exp\left\{-\gamma\pi\left(n + \frac{1}{2}\right)\right\} = 2\frac{\frac{\pi\gamma}{2}}{\sinh\left(\frac{\pi\gamma}{2}\right)}$$

The calculation of the geometrical series is quite analogous to the procedure of Example 8.1. Thus we obtain the result

$$I = \frac{4}{\beta} \cos\left(\frac{l\pi}{\alpha}\epsilon_f - \frac{\pi}{4}\right) \frac{e^{\frac{l\pi^2}{\alpha\beta}}}{\sinh\left(\frac{l\pi^2}{\alpha\beta}\right)}$$

Example 14.11: Ultrarelativistic Fermi gas

We want to study the thermodynamic properties of an ultrarelativistic ideal Fermi gas. Ultrarelativistic particles have the energy–momentum relationship $\epsilon = |\vec{p}|c$, which follows from the general formula $\epsilon = (p^2c^2 + m^2c^4)^{1/2}$ for vanishing rest mass.

While there are certain bosons with this energy–momentum relation (e.g., photons, phonons, and plasmons), the number of fermions with vanishing rest mass seems to be rather small. It is still not clear whether there are any fermions with vanishing rest mass. For instance, one can assert only an upper bound for the rest mass of the neutrino which has relatively large measurement errors, $m_\nu < 8$ eV. On the other hand, the ultrarelativistic Fermi gas can be used as a model system for a hot gas of fermions with nonvanishing rest mass, if the average momenta in the gas are large compared to mc; i.e., if the average thermal energy kT is large compared to the rest mass mc^2.

From relativistic quantum mechanics it is known that one can create pairs of particles and antiparticles (e.g., e^- and e^+) out of the vacuum at the expense of the energy $2mc^2$. These creation (and annihilation) processes will play a major role in an ultrarelativistic Fermi gas ($kT \gg mc^2$). Therefore, we must not consider a gas of Fermi particles alone; rather, we have to add the corresponding antiparticles. The vacuum represents the particle reservoir of the grand canonical ensemble, and particles and antiparticles are always exchanged with this reservoir via creation and annihilation processes.

Thus, we deal with a mixture of two ideal Fermi gases, between which "chemical" reactions are possible. In the case of the ultrarelativistic Bose gas it was not necessary to consider the antiparticles explicitly, since particles and antiparticles are identical in the more important applications (photons and phonons).

As a concrete example, we consider a hot gas of electrons and positrons. The logarithm of the grand partition function consists of two parts,

$$\ln \mathcal{Z}(T, V, z_+, z_-) = \sum_{\epsilon_+} \ln(1 + z_+ \exp\{-\beta\epsilon_+\}) + \sum_{\epsilon_-} \ln(1 + z_- \exp\{-\beta\epsilon_-\})$$

The sums run over the one-particle states of free electrons and positrons. The term $\ln \mathcal{Z}$ depends now on two fugacities z_+ and z_- or two chemical potentials μ_+ and μ_-, respectively, which are related to the mean particle numbers N_+ and N_- of particles and antiparticles via

$$N_+ = \sum_{\epsilon_+} \frac{1}{z_+^{-1} \exp\{\beta\epsilon_+\} + 1} \qquad N_- = \sum_{\epsilon_-} \frac{1}{z_-^{-1} \exp\{\beta\epsilon_-\} + 1} \tag{14.128}$$

Physically, it would not be sensible to fix all particle numbers N_+ and N_- separately and then determine the chemical potentials μ_+ and μ_-. In thermodynamic equilibrium the mean particle numbers will change via the continuously occurring creation and annihilation processes. Moreover, they may strongly fluctuate.

The changes dN_+ and dN_- of the two particle numbers are related by the equation

$$dN_+ = dN_-$$

If we write the reaction equation (for electrons and positrons) in the form

$$e^+ + e^- \rightleftharpoons \text{reaction products} + \Delta E \tag{14.129}$$

we observe that an antiparticle is also created and annihilated with each particle. Here the reaction products (e.g., photons) play no role, as long as we do not explicitly take them into account in the gas. From Equation (14.129) it follows that the chemical potentials of particles and antiparticles have to be equal (with opposite sign, cf. Chapter 3), since reaction products like photons do not carry a chemical potential,

$$\mu_+ + \mu_- = 0, \qquad z_+ z_- = 1 \tag{14.130}$$

The particle numbers N_+ and N_- are indeed not independent of each other, and there are not two independent fugacities, but actually only one. However, instead of N_+ and N_- one can fix the difference $N = N_+ - N_-$, the particle surplus, since it is not influenced by the creation and annihilation processes:

$$N = N_+ - N_- = \sum_{\epsilon_+ > 0} \frac{1}{z_+^{-1} \exp\{\beta\epsilon_+\} + 1} - \sum_{\epsilon_- > 0} \frac{1}{z_-^{-1} \exp\{\beta\epsilon_-\} + 1} \tag{14.131}$$

From this equation one has to determine the fugacity z, taking into account Equation (14.130). We can provide the system with a certain surplus N of particles, which does not change via pair creation or annihilation, but the mean particle numbers N_+ and N_- cannot be controlled.

We want to expand the result (14.130) and simultaneously explain it quantum mechanically.

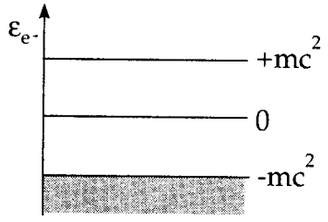


Figure 14.15. Energy spectrum of the free Dirac equation.

To this end, we consider the energy spectrum of the free Dirac equation (see Figure 14.15). In the ultrarelativistic case we must of course let $m \to 0$. As one knows, in this spectrum there are also states of negative energy $\epsilon \leq -mc^2$ besides the states of positive energy $\epsilon \geq mc^2$. One can now describe particles and antiparticles in the spectrum simultaneously, if one assumes that in the vacuum, without particles, all states of the negative energy continuum are occupied by (unobservable) electrons.

In this picture missing electrons in the negative continuum (holes) are to be interpreted as positrons (antiparticles). Let us now consider the general expression for the mean occupation number for Fermi particles:

$$\langle n_\epsilon \rangle = \frac{1}{\exp\{\beta(\epsilon - \mu)\} + 1} \tag{14.132}$$

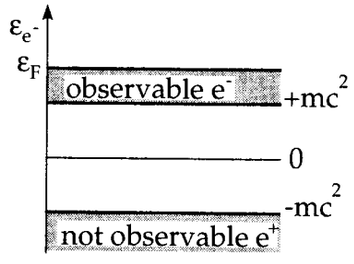


Figure 14.16. Spectrum of an electron gas at $T = 0$.

In the derivation of this occupation number no restriction for the allowed one-particle energies was made, and thus we can expect that Equation (14.132) should correctly reproduce the occupation of all electron states. For $T = 0$ and $\mu = +mc^2$ we have exactly a distribution as shown in Figure 14.16, since then expression (14.132) has the form $\Theta(mc^2 - \epsilon)$. The free Dirac equation has no solutions in the range $-mc^2 \leq \epsilon \leq +mc^2$, and thus there are no occupied states inside the interval. The minimum energy an observable (real) electron has to have is thus $\epsilon = \mu = +mc^2$.

If the Dirac equation with an external potential has bound solutions in the interval $-mc^2 \leq \epsilon \leq +mc^2$, the bound states above the lower continuum are successively filled with the observable electrons. The chemical potential at $T = 0$ is just equal to the energy of the highest occupied state.

Even then, Equation (14.132) correctly describes the physical situation. If there are further unoccupied states above the highest occupied state, a free electron without kinetic energy ($\epsilon = +mc^2$) can be captured by the system, because $\mu < mc^2$. The energy difference $mc^2 - \mu$ is released.

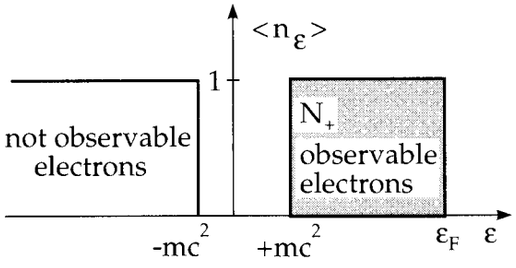


Figure 14.17. $\langle n_\epsilon \rangle$ for an electron gas at $T = 0$.

For an electron gas with N_+ electrons and a Fermi energy $\epsilon_f > mc^2$ we have at $T = 0$ the situation shown in Figure 14.17. This occupation of the electron states is correctly described by Equation (14.132), if we replace μ by the Fermi energy ϵ_f of the electrons.

If we now increase the temperature of the electron gas, at first electrons near the Fermi energy are excited into higher states $\epsilon > \epsilon_f$. This occurs in an energy range of approximate width kT around the Fermi energy.

However, if the temperature is of the order $2mc^2$, more and more electrons from the lower continuum can be excited into free states $\epsilon > \epsilon_f$. These electrons leave holes in the lower continuum, which represent observable positrons. The number of observable electrons has also increased. The difference $N_+ - N_-$, however, is the same as before. The negative energy of the holes $\epsilon_{\text{holes}} < -mc^2$ is simply related to the positive energy of the corresponding positron via $\epsilon_{e^+} = -\epsilon_{\text{hole}}$.

The number of observable electrons and positrons can be calculated as follows:

$$N_+ = \sum_{\epsilon>0} \langle n_\epsilon \rangle , \qquad N_- = \sum_{\epsilon<0} (1 - \langle n_\epsilon \rangle) \tag{14.133}$$

with $\langle n_\epsilon \rangle$ given by Equation (14.132) and $\mu = \mu_+$ as the chemical potential of the electrons (particles). As one observes, only the chemical potential of the electrons (particles) appears in this interpretation of particles and antiparticles, which is due to Dirac. On the other hand, comparing Equations (14.133) and (14.129) we can establish a connection with the picture of two different Fermi gases, between which chemical reactions are possible. Obviously, the positive electron states correspond exactly to the free electron states ϵ_+ in Equation (14.129). The unoccupied electron states of negative energy $\epsilon < 0$ have to be identified with the occupied positron states with positive energy $\epsilon_- > 0$. The expression for N_- can now be transformed:

$$\begin{aligned} N_- &= \sum_{\epsilon<0} \left(1 - \frac{1}{z^{-1} \exp\{\beta\epsilon\} + 1} \right) \\ &= \sum_{\epsilon<0} \frac{z^{-1} \exp\{\beta\epsilon\}}{z^{-1} \exp\{\beta\epsilon\} + 1} \\ &= \sum_{\epsilon<0} \frac{1}{z \exp\{-\beta\epsilon\} + 1} \end{aligned} \tag{14.134}$$

Furthermore, the energy spectrum of the free Dirac equation is symmetric around $\epsilon = 0$. Thus, one may substitute $\epsilon \to -\epsilon_-$ in Equation (14.134) and instead of counting electrons with negative energy one counts present positrons with positive energy,

$$N_- = \sum_{\epsilon_->0} \frac{1}{z \exp\{\beta\epsilon_-\} + 1}$$

A comparison with Equation (14.129) now yields in fact $z = z_-^{-1}$; i.e., $\mu_+ = -\mu_-$, in agreement with Equation (14.131). Both interpretations yield the same results, but in some

cases Dirac's particle–hole picture is more convenient. For instance, the particle excess in this picture is simply

$$N = N_+ - N_- = \sum_{\epsilon>0} \langle n_\epsilon \rangle - \sum_{\epsilon<0} (1 - \langle n_\epsilon \rangle)$$
$$= \sum_{\epsilon} \langle n_\epsilon \rangle - \sum_{\epsilon<0} 1 = \sum_{\epsilon} \langle n_\epsilon \rangle - \sum_{\epsilon} \langle n_\epsilon \rangle^{\text{vac}}$$

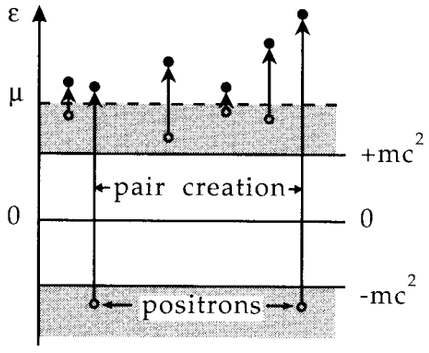


Figure 14.18. Possible processes in the electron gas at $kT \approx 2mc^2$.

The particle excess is thus always given by the difference between the total number of all electrons (observable and unobservable) and the vacuum state. Here the role of the vacuum without observable particles as a reference state becomes especially obvious. Only the deviations from the vacuum state are observable.

Let us add a comment at this place. The whole consideration can also be performed in Dirac's particle–hole picture, if the roles of particles and antiparticles are reversed. For instance, electrons would then have to be identified with holes in the negative energy continuum of the positrons. The reason is the invariance of the free Dirac equation under charge conjugation, as long as there are no electromagnetic fields present. For sake of completeness we explicitly denote both possibilities:

particles=electrons (index+), antiparticles=positrons (index −):

$$N_+ = \sum_{\epsilon>0} \frac{1}{\exp\{\beta(\epsilon - \mu_+)\} + 1},$$
$$N_- = \sum_{\epsilon<0} \left(1 - \frac{1}{\exp\{\beta(\epsilon - \mu_+)\} + 1}\right) \qquad \textbf{(14.135)}$$

particles=positrons (index −), antiparticles=electrons (index+):

$$N_+ = \sum_{\epsilon<0} \left(1 - \frac{1}{\exp\{\beta(\epsilon - \mu_-)\} + 1}\right), \qquad N_- = \sum_{\epsilon>0} \frac{1}{\exp\{\beta(\epsilon - \mu_-)\} + 1} \qquad \textbf{(14.136)}$$

Of course, Equations (14.135) and (14.136) are identical with $\mu_+ = -\mu_-$.

However, the way of consideration in Dirac's particle–hole picture presented here has a disadvantage, which should be mentioned. By marking the electrons as particles (or the

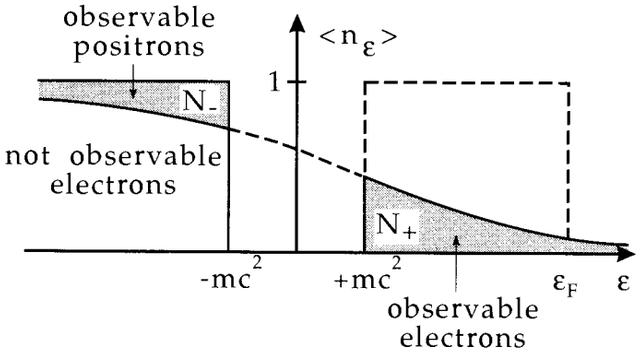


Figure 14.19. $\langle n_k \rangle$ for an electron gas at $kT \approx 2mc^2$.

positrons as particles, respectively) the symmetry of the theory with respect to charge conjugation is somewhat obscured. In the particle–hole picture antiparticles do not appear explicitly, but are replaced by unoccupied states of negative energy. On the other hand, our initial idea of two independent Fermi gases, which react chemically, is completely symmetric in particles and antiparticles.

For fermions it does not matter which representation one uses, as long as one consistently keeps to it. For bosons, which have the same energy spectrum as the fermions, a consistent particle–hole picture is not possible, since for them the Pauli principle is not valid. In the case of fermions (electron gas) the (unobservable) electrons of the negative energy continuum prevent a "falling down" of electrons with positive energy towards infinitely negative energies under steady energy gain. For bosons, however, this process cannot be prevented, and one has to refer to the initial picture of two gases. Equation (14.130) still holds for bosons if the $+1$ in the denominator is replaced by -1.

We now want to proceed with the calculation. At first we rewrite the sums in Equation (14.125) and (14.131) in terms of integrals, for which we need the state density $g(\epsilon)$ of ultrarelativistic particles (see Equation (13.6), with degeneracy factor g),

$$g(\epsilon) = g\,\frac{4\pi V}{h^3c^3}\,\epsilon^2$$

$$\ln \mathcal{Z} = g\,\frac{4\pi V}{h^3c^3}\int_0^\infty \epsilon^2\,d\epsilon\,\left[\ln\left(1+\exp\{-\beta(\epsilon-\mu)\}\right)+\ln\left(1+\exp\{-\beta(\epsilon+\mu)\}\right)\right]$$

or after integration by parts,

$$\ln \mathcal{Z} = g\,\frac{4\pi V}{h^3c^3}\,\frac{\beta}{3}\int_0^\infty \epsilon^3\,d\epsilon\left[\frac{1}{\exp\{\beta(\epsilon-\mu)\}+1}+\frac{1}{\exp\{\beta(\epsilon+\mu)\}+1}\right] \tag{14.137}$$

$$\begin{aligned} N &= N_+ - N_- \\ &= g\,\frac{4\pi V}{h^3c^3}\int_0^\infty \epsilon^2\,d\epsilon\left[\frac{1}{\exp\{\beta(\epsilon-\mu)\}+1}-\frac{1}{\exp\{\beta(\epsilon+\mu)\}+1}\right] \end{aligned} \tag{14.138}$$

where we simply write μ for the chemical potential μ_+ of the particles and $-\mu$ for μ_- of the antiparticles. The integrals in Equations (14.137) and (14.138) fortunately can be evaluated with analytical means, without using the special functions $f_n(z)$. We substitute $x = \beta(\epsilon-\mu)$ in the first term and $y = \beta(\epsilon+\mu)$ in the second. We then obtain for Equation (14.137)

$$\ln \mathcal{Z} = \frac{g4\pi V}{c^3h^3}\,\frac{\beta}{3}\left[\beta^{-1}\int_{-\beta\mu}^\infty dx\,\frac{\left(\frac{x}{\beta}+\mu\right)^3}{e^x+1}+\beta^{-1}\int_{\beta\mu}^\infty dy\,\frac{\left(\frac{y}{\beta}-\mu\right)^3}{e^y+1}\right]$$

We now rewrite the integrals so that we can integrate from 0 to ∞,

$$\begin{aligned} \ln \mathcal{Z} = \frac{g4\pi V}{c^3h^3}\,\frac{\beta^{-3}}{3}\Bigg[&\int_0^\infty dx\,\frac{(x+\beta\mu)^3}{e^x+1}+\int_0^\infty dy\,\frac{(y-\beta\mu)^3}{e^y+1} \\ &+\int_{-\beta\mu}^0 dx\,\frac{(x+\beta\mu)^3}{e^x+1}-\int_0^{\beta\mu} dy\,\frac{(y-\beta\mu)^3}{e^y+1}\Bigg] \end{aligned}$$

The first two integrals can be directly combined, the last two after the substitution $y = -x$.

$$\ln \mathcal{Z} = \frac{g4\pi V}{c^3h^3}\,\frac{\beta^{-3}}{3}\left[\int_0^\infty dx\,\frac{2x^3 + 6x(\beta\mu)^2}{e^x + 1} + \int_{-\beta\mu}^0 dx(x + \beta\mu)^3\left(\frac{1}{e^x + 1} + \frac{1}{e^{-x} + 1}\right)\right]$$

If we now consider $(e^x + 1)^{-1} + (e^{-x} + 1)^{-1} = 1$, we find

$$\ln \mathcal{Z} = \frac{g4\pi V}{c^3h^3}\,\frac{\beta^{-3}}{3}\left[2\int_0^\infty dx\,\frac{x^3}{e^x + 1} + 6(\beta\mu)^2\int_0^\infty dx\,\frac{x}{e^x + 1} + \int_0^{\beta\mu} dz z^3\right] \tag{14.139}$$

In the last integral we have substituted $z = x + \beta\mu$. Analogously, we now treat Equation (14.138):

$$\begin{aligned} N &= \frac{g4\pi V}{c^3h^3}\left[\beta^{-1}\int_{-\beta\mu}^\infty dx\,\frac{\left(\frac{x}{\beta} + \mu\right)^2}{e^x + 1} - \beta^{-1}\int_{\beta\mu}^\infty dy\,\frac{\left(\frac{y}{\beta} - \mu\right)^2}{e^y + 1}\right] \\ &= \frac{g4\pi V}{c^3h^3}\,\beta^{-3}\left[\int_0^\infty dx\,\frac{(x + \beta\mu)^2}{e^x + 1} - \int_0^\infty dy\,\frac{(y - \beta\mu)^2}{e^y + 1}\right. \\ &\quad \left. + \int_{-\beta\mu}^0 dx\,\frac{(x + \beta\mu)^2}{e^x + 1} + \int_0^{\beta\mu} dy\,\frac{(y - \beta\mu)^2}{e^y + 1}\right] \\ &= \frac{g4\pi V}{c^3h^3}\,\beta^{-3}\left[4\beta\mu\int_0^\infty dx\,\frac{x}{e^x + 1} + \int_0^{\beta\mu} dz z^2\right] \end{aligned} \tag{14.140}$$

In the last line we have again combined the two last integrals from the preceding line and substituted $z = x + \beta\mu$. Note that this can be done only for $N_+ - N_-$, and not for $N_+ + N_-$.

For the total particle number there is no simple analytical solution, as well as for N_+ and N_- separately. One can calculate these quantities with the help of the $f_n(z)$ functions.

The integrals occurring in Equations (14.139) and (14.140) can be expressed with the help of Equation (14.27):

$$\begin{aligned} \int_0^\infty dx\,\frac{x^3}{e^x + 1} &= \Gamma(4)f_4(1) = 6\left(1 - \frac{1}{2^3}\right)\zeta(4) = \frac{7\pi^4}{120} \\ \int_0^\infty dx\,\frac{x}{e^x + 1} &= \Gamma(2)f_2(1) = 1\left(1 - \frac{1}{2}\right)\zeta(2) = \frac{\pi^2}{12} \end{aligned} \tag{14.141}$$

Therewith we have the results

$$\begin{aligned} \ln \mathcal{Z}(T, V, \mu) &= \frac{g4\pi V}{h^3c^3}\,\frac{\beta^{-3}}{3}\left[2\frac{7\pi^4}{120} + 6(\beta\mu)^2\frac{\pi^2}{12} + \frac{1}{4}(\beta\mu)^4\right] \\ &= \frac{gV}{h^3c^3}\,\frac{4\pi}{3}(kT)^3\left[\frac{7\pi^4}{60} + \left(\frac{\mu}{kT}\right)^2\frac{\pi^2}{2} + \left(\frac{\mu}{kT}\right)^4\frac{1}{4}\right] \\ N(T, V, \mu) &= \frac{g4\pi V}{h^3c^3}\,\beta^{-3}\left[4\beta\mu\frac{\pi^2}{12} + \frac{1}{3}(\beta\mu)^3\right] \\ &= \frac{g4\pi V}{h^3c^3}(kT)^3\left[\left(\frac{\mu}{kT}\right)\frac{\pi^2}{3} + \frac{1}{3}\left(\frac{\mu}{kT}\right)^3\right] \end{aligned}$$

From Equation (14.141) one can in principle calculate the internal energy via $U = -\partial(\ln \mathcal{Z})/\partial\beta$, but the following consideration is simpler:

$$U = U_+ + U_- = \sum_{\epsilon_+} \langle n_\epsilon \rangle_+ \, \epsilon_+ + \sum_{\epsilon_-} \langle n_\epsilon \rangle_- \, \epsilon_-$$

$$= \frac{g 4\pi V}{h^3 c^3} \int_0^\infty \epsilon^3 \, d\epsilon \left[\frac{1}{\exp\{\beta(\epsilon - \mu)\} + 1} + \frac{1}{\exp\{\beta(\epsilon + \mu)\} + 1} \right]$$

This is identical to Equation (14.137) up to a factor $\beta/3$, so that

$$\ln \mathcal{Z} = \frac{pV}{kT} = \frac{\beta}{3} U$$

or

$$p = \frac{1}{3} \frac{U}{V} = g \frac{(kT)^4}{(\hbar c)^3} \frac{1}{3} \left[\frac{7\pi^2}{120} + \left(\frac{\mu}{kT} \right)^2 \frac{1}{4} + \left(\frac{\mu}{kT} \right)^4 \frac{1}{8\pi^2} \right] \qquad \textbf{(14.142)}$$

By the way, the first term in Equation (14.142) is quite similar to the Stefan–Boltzmann law for the ultrarelativistic photon gas ($\mu = 0$).

The density of the particle surplus is

$$\frac{N}{V} = \frac{N_+ - N_-}{V} = \frac{g}{6} \left(\frac{kT}{\hbar c} \right)^3 \left[\left(\frac{\mu}{kT} \right) + \left(\frac{\mu}{kT} \right)^3 \frac{1}{\pi^2} \right]$$

The free energy density follows from $\frac{F}{V} = \frac{N}{V}\mu - p$ as

$$\frac{F}{V} = g \frac{(kT)^4}{(\hbar c)^3} \left[\frac{1}{8\pi^2} \left(\frac{\mu}{kT} \right)^4 + \frac{1}{12} \left(\frac{\mu}{kT} \right)^2 - \frac{1}{3} \frac{7\pi^2}{120} \right]$$

With this one can also calculate the entropy density $\frac{S}{V} = \frac{1}{T} \left(\frac{U}{V} - \frac{F}{V} \right)$:

$$\frac{S}{V} = gk \left(\frac{kT}{\hbar c} \right)^3 \left[\frac{7\pi^2}{90} + \frac{1}{6} \left(\frac{\mu}{kT} \right)^2 \right]$$

Supplement: Natural units

At this point, we want to add a few comments regarding a system of units which is frequently used in modern physics. The so–called *natural units* are fixed by the definition

$$\hbar = c = k = 1 \tag{14.143}$$

This system of units has many advantages from the theoretician's point of view. It supports the relativistical covariant formulation of theories and saves us from dragging along the constant factors $\hbar$, c, and k, which occur very often in relativistic quantum mechanics and quantum statistics. It is, in particular, useful for very small ($x \approx$ fm), highly energetic ($E/N \approx$ GeV), and relativistic ($v \approx c$) systems. As a disadvantage one has to note that quite different physical measurables (e.g., mass and temperature, or angular momentum and velocity) have the same unit and carry—for daily life quantities—very clumsy numbers.

Planck's constant, the velocity of light, and Boltzmann's constant have the values—in international SI units (basic units: meter, kilogram, second, Ampère, Kelvin, candela, mol), or in practical nuclear physics units (1 eV=1.6022 $\cdot 10^{-19}$ J, 1 fm=10^{-15} m), respectively,

$$\begin{aligned}
\hbar &= \frac{h}{2\pi} = 1.0546 \cdot 10^{-34}\ \text{Js} = 6.5821 \cdot 10^{-16}\ \text{eV s} \\
c &= 2.9979 \cdot 10^{8}\ \text{m s}^{-1} = 2.9979 \cdot 10^{23}\ \text{fm s}^{-1} \\
k &= 1.3807 \cdot 10^{-23}\ \text{J K}^{-1} = 0.86174 \cdot 10^{-4}\ \text{eV K}^{-1}
\end{aligned} \tag{14.144}$$

The three constants contain four different units, namely eV, s, fm, and K. Via Equations (14.143), three of these units can be eliminated. As the independent unit one mostly chooses eV (better MeV) or fm. These two units are related to each other via the relation

$$\hbar c = 197.327\ \text{MeV fm} = 1 \tag{14.145}$$

which is very important for converting the units. It is mostly sufficient to remember the approximate value $\hbar c \approx 200$ MeV fm.

Via the definition $c = 1$, lengths and times have the same dimension, namely fm (or MeV^{-1}). The quantity $t = 1$ fm corresponds to the time during which the light travels a distance 1 fm. Consequently, velocities become dimensionless and are given as fractions of c. It is clear that this supports the relativistic formulation with four vectors, since now all components of $x^\mu = (ct, \vec{r})$ are measured in the same units and the additional factor c drops out everywhere. Quite analogously, the definition $\hbar = 1$ causes energies and frequencies ($E = \hbar\omega$), as well as momenta and wave vectors ($\vec{p} = \hbar\vec{k}$) to have the same unit MeV (or fm^{-1}). The components of the momentum four vector $p^\mu = (\frac{E}{c}, \vec{p})$ then have the same unit, fm^{-1} (or MeV), and the scalar product $x_\mu p^\mu$, which often appears as an argument in plane waves, is dimensionless, as is the angular momenta, which is measured in multiples of $\hbar$.

This system of units can also be implemented in electrodynamics. For this purpose, however, one first has to fix the system of units for electrodynamics itself. In Gauss' system,

the square of the elementary charge reads

$$e^2 = 1.44\,\text{MeV fm} = \frac{1}{137} \qquad \text{or} \qquad \alpha = \frac{e^2}{\hbar c} = \frac{1}{137} \tag{14.146}$$

Therefore, in natural units e^2 is identical to the fine structure constant α (which is independent of the system of units). We have to note that in electrodynamics (especially in the covariant formulation) one often uses the Heaviside–Lorentz system. In this system we have $e^2|_{HL} = 4\pi e^2|_{\text{Gauss}}$, and thus one often finds an additional factor 4π in Equation (14.146), $\alpha = \left.\frac{e^2}{4\pi}\right|_{HL} = \frac{1}{137}$ with $\hbar c = 1$. The advantage of the Heaviside–Lorentz system is that the potential equations

$$\Box A^\mu = 4\pi\ j^\mu|_{\text{Gauss}} \tag{14.147}$$

no longer contain the factor 4π;

$$\Box A^\mu = j^\mu|_{HL} \tag{14.148}$$

On the other hand, the Coulomb potential reads

$$\left.\frac{e^2}{r}\right|_{\text{Gauss}} \rightarrow \left.\frac{e^2}{4\pi r}\right|_{HL} \tag{14.149}$$

In modern quantum field theory (QED, QCD) one refers almost exclusively to the Heaviside–Lorentz system.

Finally, the temperature unit *Kelvin* can be eliminated by the definition $k = 1$. Temperatures are measured like energies in natural units ($E = kT$). Entropy and heat capacity, which have the same unit as Boltzmann's constant, are dimensionless in natural units and are measured in multiples of k.

15 Applications of Relativistic Bose and Fermi Gases

Quark–gluon plasma in the Big Bang and in heavy-ion collisions

In elementary particle physics one has the opinion nowadays that quantum chromodynamics (QCD) is the fundamental theory of strong interactions (see Volume 7 of this series). All hadrons (strongly interacting particles like the neutron and the proton) consist of the elementary quarks in this theory. Besides an electrical charge (multiples of $\frac{1}{3}e$), quarks carry a so-called color charge (from the Greek *chroma* ($\chi\rho\tilde{\omega}\mu\alpha$), meaning color). The color charges are the sources of the color field, just as the electrical charges are sources for the electric field. Quarks interact via the color field. The main difference between electric charge and color charge is that the latter is a vectorial quantity with three components, which are usually called *red, green*, and *blue*.

In mathematical terms, quantum electrodynamics (QED) is a gauge theory based on the gauge group $U(1)$ (unitary group in one dimension, see Volume 5 of this series), and QCD is a gauge theory with gauge group $SU(3)$ (special unitary group in three dimensions). The quanta of the color field are called *gluons*, in analogy to the photons in QED. However, while the photons (or the electromagnetic field) do not carry electrical charge, the gluons (or the color field) have a color charge themselves (or better, a color transition charge). For instance, a red quark can transform into a green quark under emission of a gluon with a certain color charge, while the electrical charge of a particle does not change when it emits a photon.

In QCD a lot of pecularities occur which are not known in QED. Unfortunately, a solution of the fundamental equations of QCD is still impossible. Therefore, one has to rely on models, which can, however, be partially confirmed by computer simulations (lattice gauge theory). An essential difference in comparison to electrodynamics is, e.g., the rise of the color potential between two color charges proportional to a power of the mutual distance, $\propto r^{\alpha}$, while the analogous Coulomb potential decreases like $1/r$. (See Figure 15.1.) This means that it would take an infinite amount of energy to completely separate two (classical) color charges. However, quantum mechanically, quark–antiquark pairs are created out of the vacuum, if the distance is of the order of a few fm. At such distances the field energy is larger than twice the mass (rest energy) of the quark, and it is

energetically more favorable for the system to create a quark–antiquark pair than to maintain the field.

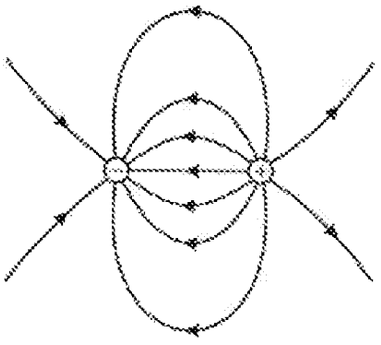


Figure 15.1. Electric field.

This implies that color fields between two color charges are confined to a small tube, because the (virtual or real) gluons also cannot move far away from the respective color charges, since they are charged themselves (see Figure 15.2). In other words, color fields cannot permeate into the vacuum. For color fields, the vacuum is an ideal dielectrical material, in which counter charges are induced via the (vacuum) polarization, which in turn prevent the penetration of the color fields.

The small color hose between two color charges is commonly called a *color flux tube*.

A simple consideration shows that such a tube acts like a rubber band. To draw the two charges apart requires a constant force which is independent of the distance, corresponding to a linear potential $V \propto r$.

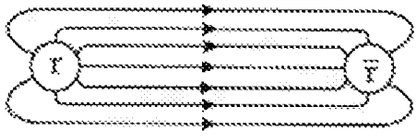


Figure 15.2. Color field.

An important consequence of this property is that there are only neutral color (white) objects in nature, and single color charges (quarks or gluons) are not observable (*confinement*). Since there are obviously no free quarks, perturbation theory, which uses plane waves as basis states and is very successful in QED, becomes inapplicable in QCD. Only at very high energies (very small distances) does QCD perturbation theory yield useful results which can be experimentally checked. At very small distances the confining potential becomes small, and the quarks behave approximately like free particles. One calls this property of quarks *asymptotic freedom*.

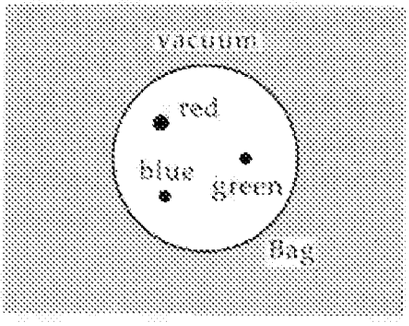


Figure 15.3. MIT bag model.

A simple but nevertheless very successful model for hadrons is based on this fact, namely the MIT bag model (Figure 15.3). After the original ideas of Bogolyubov, this model was developed by a group of physicists at the Massachusetts Institute of Technology (MIT) in the 1970s. In this model, hadrons are bags in the vacuum, in which quarks may move freely but cannot penetrate the vacuum due to certain boundary conditions at the surface.

To get a neutral color proton or neutron, the bag is filled with three quarks (red, green, blue), which together are color neutral (white). However, it can be shown that it is necessary to introduce several kinds of quarks (*flavors*) to describe the variety of hadrons. The existence of at least five different quarks is sure nowadays, for another there are strong theoretical indications.* One calls them *u*(up), *d*(down), *s*(strange), *c*(charm), *b*(bottom) or *b*(beauty), and *t*(top) or *t*(truth), respectively.

*Remark: All quarks except the top have been unambiguously detected. Recent experiments at Fermilab: F. Abe et al., Phys. Rev. Lett. 73, 225 (1994).

A neutron, for instance, has the quark content (udd) and a proton has (uud). However, the masses of the neutron and the proton ($m \approx 1$ GeV) originate only to a tiny fraction from the masses of the quarks, which are supposed to be relatively small, $m_u \approx 5$ MeV, $m_d \approx 10$ MeV. The largest part stems from the kinetic energy of the quarks in the bag.

On the other hand, the free motion of the nearly massless quarks in the bag causes a Fermi pressure, which we have already discussed in connection with the ideal Fermi gas. Thus, a bag would not be stable, but would try to expand. One therefore additionally assumes that the vacuum exerts an external pressure on the bag, which is called *bag pressure* and abbreviated by the letter B. Such an external pressure, additionally introduced by hand, is of course necessary only because one cannot treat QCD exactly; otherwise the color fields would care for the confinement.

This crude model can already explain the occurrence of well-ordered hadronic families (mass multiplets, see *Quantum Mechanics: Symmetries*, by W. Greiner and B. Müller). With a few additional refinements (color fields in perturbation theory) one can even reproduce quite satisfactorily the mass splitting inside a multiplett.

In an atomic nucleus at normal nuclear density ($\rho_0 \approx 0.17\ \mathrm{fm}^{-3}$), the single nucleons (bags) with radius $R \approx 1$ fm are well separated. However, it is reasonable to assume that at large densities and high temperatures the bags overlap and melt into a larger area, where quarks and gluons can move nearly freely. One calls such a state of nearly free quarks and gluons in thermodynamic equilibrium a *quark–gluon plasma*. Today it is commonly assumed that this state of matter existed in the first milliseconds after the Big Bang, and may also exist in the interior of quasars or very heavy neutron stars. In recent times some have tried to create such a quark–gluon plasma under laboratory conditions in high-energy nucleus–nucleus collisions. To this end, however, heavy-ion beams of extraordinarily high energy are necessary. Only since 1986 have such beams been available at the SPS accelerator of the European Nuclear Research Centre CERN in Geneva.

We do not want to go into the details of the many problems which still have to be solved in this context, e.g., which fraction of the kinetic energy of the nuclei is transformed into thermal or compressional energy, respectively, which are the experimental signatures for the creation of the plasma, or how it finally decays into hadrons. However, with a few simple considerations in the framework of quantum statistics we can obtain an overview of the main properties of a quark–gluon plasma.

To this end, we treat quarks and gluons as ultrarelativistic Fermi or Bose gases, respectively. Of course, this can only be a crude approximation, since quarks interact strongly even in the plasma. However, such an estimate will yield the order of magnitude of the pressure, the energy density, etc., in the plasma. For the contribution of the gluons to the pressure or to the energy density, respectively, we find using Equation (13.66), in natural units

$$p_G = \frac{1}{3}\left.\frac{U}{V}\right|_G = g_G \frac{\pi^2}{90} T^4 \tag{15.1}$$

Here g_G is the degeneracy factor of the gluons. Gluons have (like photons) two spin projections (polarizations). However, since there are three independent components of

the color charge, and consequently $3 \cdot 3 - 1$ generators of $SU(3)$ (eight different color transition charges, see *Quantum Chromodynamics*, by W. Greiner and A. Schäfer), we have $g_G = 2 \cdot 8 = 16$. The entropy density can be readily calculated with the help of Equation (13.68):

$$s_G = \frac{S_G}{V} = g_G \frac{4\pi^2}{90} T^3 \tag{15.2}$$

Analogously, the contribution of quarks and antiquarks to the pressure is given by Example 14.11 (in natural units):

$$p_Q = \frac{1}{3} \frac{U}{V}\bigg|_Q = \frac{g_Q}{3} T^4 \left[\frac{7\pi^2}{120} + \frac{1}{4} \left(\frac{\mu}{T} \right)^2 + \frac{1}{8\pi^2} \left(\frac{\mu}{T} \right)^4 \right] \tag{15.3}$$

The degeneracy factor of quarks is composed of the product of the two spin projections, the three colors and the two quark flavors u and d under consideration (for ordinary nuclear matter without exotic particles containing strange quarks, charm quarks, etc.); i.e., $g_Q = 2 \cdot 3 \cdot 2 = 12$. The entropy density is

$$s_Q = \frac{S_Q}{V} = g_Q T^3 \left[\frac{7\pi^2}{90} + \frac{1}{6} \left(\frac{\mu}{T} \right)^2 \right] \tag{15.4}$$

To determine the chemical potential μ of the quarks, the equation

$$n = \frac{N}{V} = \frac{g_Q}{6} T^3 \left[\frac{\mu}{T} + \frac{1}{\pi^2} \left(\frac{\mu}{T} \right)^3 \right] \tag{15.5}$$

is required. This equation relates the quark surplus $n = n_Q - n_{\overline{Q}}$ to the chemical potential. With respect to the creation of a quark–gluon plasma in high-energy heavy-ion collisions it is convenient to write the quark surplus density in terms of the density of the nucleons. The density of the nucleons n_{nuc}, however, is just one third of the quark density, since three quarks initially constitute one nucleon. It thus holds that

$$n_{\text{nuc}} = \frac{1}{3} n \tag{15.6}$$

If we define the dimensionless quantities $x = \mu/T$ and $y = \frac{18}{g_Q} n_{\text{nuc}}/T^3$, Equation (15.5) becomes

$$y = x + \frac{x^3}{\pi^2} \tag{15.7}$$

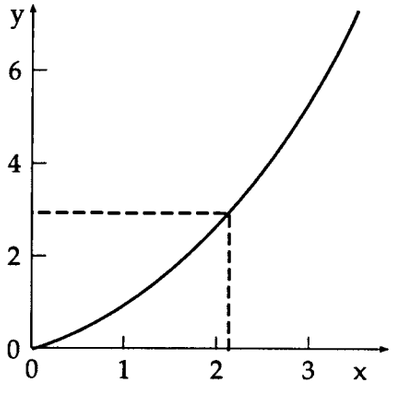


Figure 15.4. Concerning the solution of Equation (15.7).

One hopes to achieve approximately 5 times nuclear density $n_{\text{nuc}} \approx 0.85\,\text{fm}^{-3}$ and temperatures of about $T \approx 150\,\text{MeV}$ in heavy-ion collisions. This corresponds to $y \approx 2.9$. With the help of Figure 15.4, we can solve Equation (15.7) graphically, which yields $x \approx 2.05$. The chemical potential of the quarks has thus a value of approximately $\mu \approx 2.05T \approx 300\,\text{MeV}$.

However, we can even proceed a step further and determine the phase boundary of the quark–gluon plasma in the μT diagram. The plasma should be stable as long as the total

pressure $p = p_Q + p_G$ wins over the external vacuum pressure, represented by the bag constant. This leads to the estimate

$$B = p_Q + p_G = T_c^4 \left[\frac{37\pi^2}{90} + \left(\frac{\mu_c}{T_c}\right)^2 + \frac{1}{2\pi^2}\left(\frac{\mu_c}{T_c}\right)^4 \right] \tag{15.8}$$

for the phase boundary $T_c(\mu_c)$ in the μT diagram (see Figure 15.5). For $\mu_c = 0$ we have, for instance, $T_c = 0.7B^{1/4} \approx 102$ MeV, for a value $B^{1/4} = 145$ MeV (in natural units), estimated via the MIT bag model, and for $T_c = 0$ follows $\mu_c = 2.1B^{1/4} \approx 305$ MeV.

This estimate for the phase boundary is, of course, very crude, and one should reckon with a factor of 2 uncertainty.

One nevertheless observes that a chemical potential of 300 MeV and temperature of 150 MeV should be sufficient to reach the plasma state of quarks and gluons. Experiments to create such a quark–gluon plasma are currently being done at CERN.

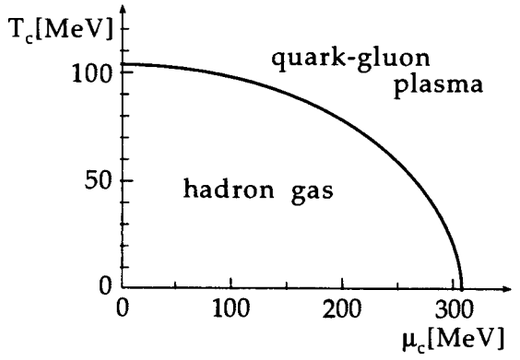


Figure 15.5. Phase boundary in the μT diagram.

Exercise 15.1: Interacting quantum gases

As one knows, a quantum state R of an interaction-free quantum gas is completely determined by specifying the occupation numbers $\{n_1, n_2, \ldots, n_r, \ldots\}$ of the discrete quantum states r with the energy ϵ_r. Its energy is the sum of all energies ϵ_r of the particles in the quantum states r,

$$E_R^{\text{free}} = \sum_r n_r \epsilon_r$$

where $\epsilon_r = \sqrt{p_r^2 + m^2}$ (in natural units) is the relativistic energy of the particle with mass m in the momentum state $\vec{p}_r$.

1) Derive an expression for the grand canonical partition function $\mathcal{Z}(T, V, z)$ of an interacting quantum gas assuming that the total interaction energy can be written in the form

$$U(V, n) = Vu(n)$$

($n = N/V$ is the particle density). Such density-dependent interactions have applications in nuclear and elementary particle physics (see the following Example).

The energy of a quantum state R then reads

$$\begin{aligned} E_R &= \sum_r n_r \epsilon_r + U \\ &= \sum_r n_r \epsilon_r + Vu(n) \end{aligned} \tag{15.9}$$

where ϵ_r represents only the kinetic and rest energy of a single particle. Its potential energy, on the other hand, is contained in the term $Vu(n)$.

2) Derive the thermodynamic state quantities

$$\overline{N} = -\left.\frac{\partial \Phi}{\partial \mu}\right|_{T,V} \quad \text{Mean particle number}$$

$$S = -\left.\frac{\partial \Phi}{\partial T}\right|_{\mu,V} \quad \text{Entropy}$$

$$\overline{E} = +\left.\frac{\partial (\Phi\beta)}{\partial \beta}\right|_{z,V} \quad \text{Mean total energy}$$

$$p = -\left.\frac{\partial \Phi}{\partial V}\right|_{\mu,T} \quad \text{Pressure}$$

via differentiation of the grand canonical potential $\Phi = -T \ln \mathcal{Z}(T, V, z)$, and check the Euler equation

$$\overline{E} - TS + pV - \mu\overline{N} = 0 \tag{15.10}$$

Solution

1) The grand canonical partition function reads

$$\mathcal{Z}(T, V, z) = \sum_{N=0}^{\infty} z^N Z(T, V, N) \tag{15.11}$$

with the fugacity $z = \exp\{\beta\mu\}$ and the canonical partition function

$$Z(T, V, N) = \sum_{R}{}' \exp\{-\beta E_R\} \tag{15.12}$$

where the prime on the sum indicates that one has to sum over all quantum states under the restriction

$$\sum_r n_r = N \tag{15.13}$$

In the grand canonical partition function this restriction drops out, since we sum over all N, and we obtain after inserting Equation (15.9) into (15.12), and the result into Equation (15.11):

$$\mathcal{Z}(T, V, \mu) = \sum_{n_1, n_2, \ldots = 0}^{\infty/1} \exp\left\{-\beta\left(\sum_r n_r(\epsilon_r - \mu) + Vu(n)\right)\right\} \tag{15.14}$$

where we have exploited $z^N = \exp\{N\beta\mu\} = \exp\{\beta \sum_r n_r \mu\}$ according to Equation (15.13). The upper summation index in Equation (15.14) indicates that infinitely many bosons can be in the quantum state r, but only one fermion, due to Pauli's principle. Thus, for bosons we have to take the index ∞, and for fermions the index 1. Here we treat both cases simultaneously.

For the further evaluation of Equation (15.14) it is necessary that the exponential function decompose into factors of the form $\exp\{-\beta n_r(\ldots)\}$. This is possible only if the term $Vu(n)$ is linear in $N = \sum_r n_r$. In general, this is not the case; $Vu(n)$ is a complicated function of N, which has to be determined after the interaction is specified. Therefore, the only possibility is to linearize $Vu(n)$ as a function of N, which can be done via a Taylor series expansion of $u(n)$ around the mean value of the particle number density $\bar{n}$:

$$u(n) = u(\overline{n}) + u'(\overline{n})(n - \overline{n}) + \cdots \tag{15.15}$$

Higher order terms are neglected due to the argument that fluctuations $n - \overline{n}$ around the mean particle number density become small in the thermodynamic limit.

In fact, we now have decomposed $U(V, n)$ into two constant terms, $U(V, \overline{n}) = Vu(\overline{n})$ and $Vu'(\overline{n})\overline{n} = u'(\overline{n})\overline{N}$, which depend only on the mean particle number $\overline{N}$, and into a term $Vu'(\overline{n})n = u'(\overline{n})N$, which is linear in $N = \sum_r n_r$. Now we can write the total energy of the quantum state R also in the form

$$E_R = \sum_r n_r(\epsilon_r + u'(\overline{n})) + U(V, \overline{n}) - u'(\overline{n})\overline{N} \tag{15.16}$$

Except for the last two (constant) terms, the energy of a single particle in the quantum state r is just $\epsilon_r + u'(\overline{n})$. Thus, each particle has a mean potential energy $u'(\overline{n})$, which originates from its interaction with other particles. One can also think of this potential energy as being due to a mean field at the position of the particle, for which reason the ansatz (15.15) corresponds exactly to the so-called *molecular field approximation* (mean-field approximation, cf. Chapter 18).

The evaluation of Equation (15.14) is now simple, since one can draw the constant terms in Equation (15.16) in front of the sum (they do not depend on the occupation numbers $n_1, n_2, \ldots$):

$$\begin{aligned}\mathcal{Z}(T, V, \mu) &= \exp\left\{-\beta\left(U(V, \overline{n}) - u'(\overline{n})\overline{N}\right)\right\} \\ &\quad \times \sum_{n_1, n_2, \ldots = 0}^{\infty/1} \exp\left\{-\beta\left[\sum_r (\epsilon_r + u'(\overline{n}) - \mu)n_r\right]\right\} \\ &= \exp\left\{-\beta\left(U(V, \overline{n}) - u'(\overline{n})\overline{N}\right)\right\} \\ &\quad \times \prod_{r=1}^{\infty}\left(\sum_{n_r=0}^{\infty/1} \exp\left\{-\beta\left[\epsilon_r + u'(\overline{n}) - \mu\right]n_r\right\}\right)\end{aligned} \tag{15.17}$$

since the exponential function in the first line of Equation (15.16) factors. The sum in brackets in the last line of Equation (15.17) is just a geometric series in the case of bosons, and even simpler, contains only two terms ($n_r = 0, 1$) in the case of fermions. Our final result thus reads

$$\begin{aligned}\mathcal{Z}(T, V, \mu) &= \exp\left\{-\beta\left(U(V, \overline{n}) - u'(\overline{n})\overline{N}\right)\right\} \\ &\quad \times \prod_{r=1}^{\infty}\begin{cases}(1 + \exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\}) & \text{Fermions} \\ (1 - \exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\})^{-1} & \text{Bosons}\end{cases}\end{aligned}$$

With the abbreviation $a = +1$ for fermions, and $a = -1$ for bosons the grand canonical potential can be written

$$\Phi = -T \ln \mathcal{Z} = -Ta \sum_r \ln(1 + a \exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\}) + U(V, \overline{n}) - \overline{N}u'(\overline{n}) \tag{15.18}$$

Note the two "additional" terms. They will play an important role in the following part of the Exercise.

2) We have

$$\overline{N} = -\left.\frac{\partial \Phi}{\partial \mu}\right|_{T,V}$$

$$= -V \left.\frac{\partial u(\overline{n})}{\partial \mu}\right|_{T,V}$$

$$+ \overline{N} \left.\frac{\partial u'(\overline{n})}{\partial \mu}\right|_{T,V} + u'(\overline{n}) \left.\frac{\partial \overline{N}}{\partial \mu}\right|_{T,V}$$

$$+ Ta \sum_r \frac{a \exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\}}{1 + a \exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\}} \left(\beta - \beta \left.\frac{\partial u'(\overline{n})}{\partial \mu}\right|_{T,V}\right)$$

From this follows

$$\overline{N}\left(1 - \left.\frac{\partial u'(\overline{n})}{\partial \mu}\right|_{T,V}\right) = -V \left.\frac{\partial u(\overline{n})}{\partial \mu}\right|_{T,V}$$

$$+ u'(\overline{n}) \left.\frac{\partial \overline{N}}{\partial \mu}\right|_{T,V}$$

$$+ a^2 \beta T \left(1 - \left.\frac{\partial u'(\overline{n})}{\partial \mu}\right|_{T,V}\right)$$

$$\times \sum_r \frac{1}{\exp\{\beta(\epsilon_r + u'(\overline{n}) - \mu)\} + a} \tag{15.19}$$

We now take into account the fact that $du = \frac{du}{dn}\, dn$, since u depends only on the particle number density. Then we have

$$\left.\frac{\partial u(\overline{n})}{\partial \mu}\right|_{T,V} = u'(\overline{n}) \left.\frac{\partial \overline{n}}{\partial \mu}\right|_{T,V} = u'(\overline{n}) \frac{1}{V} \left.\frac{\partial \overline{N}}{\partial \mu}\right|_{T,V} \tag{15.20}$$

and the first two terms in Equation (15.19) cancel. With $a^2 = 1$ and $\beta T = 1$ (in natural units), we thus obtain

$$\overline{N} = \sum_r \frac{1}{\exp\{\beta(\epsilon_r + u'(\overline{n}) - \mu)\} + a} \tag{15.21}$$

because the brackets in Equation (15.19) do not vanish in general, since $u(n)$ can be an arbitrary function. The mean occupation number can be immediately read off due to $\overline{N} = \sum_r \overline{n}_r$:

$$\overline{n}_r = \frac{1}{\exp\{\beta(\epsilon_r + u'(\overline{n}) - \mu)\} + a} \tag{15.22}$$

In comparison to the free case, only the one-particle energy was modified in the mean-field approximation: $\epsilon_r \to \epsilon_r + u'(\overline{n})$.

The entropy reads

$$S = -\left.\frac{\partial \Phi}{\partial T}\right|_{\mu,V} = -V \left.\frac{\partial u(\overline{n})}{\partial T}\right|_{\mu,V} + \overline{N} \left.\frac{\partial u'(\overline{n})}{\partial T}\right|_{\mu,V} + u'(\overline{n}) \left.\frac{\partial \overline{N}}{\partial T}\right|_{\mu,V}$$

$$+ a \sum_{r=1}^{\infty} \ln\{1 + a \exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\}\}$$

$$+ a^2 T \sum_{r=1}^{\infty} \frac{(\epsilon_r + u'(\overline{n}) - \mu)\left(-\frac{d\beta}{dT}\right) - \beta \left.\frac{\partial u'(\overline{n})}{\partial T}\right|_{\mu,V}}{\exp\{\beta(\epsilon_r + u'(\overline{n}) - \mu)\} + a}$$

As in Equation (15.20), one can show that the first and third terms cancel. With Equation (15.21) it furthermore follows that the second term cancels the last term in the numerator of the last sum. With $-\frac{d\beta}{dT} = \frac{1}{T^2}$, the result reads

$$S = a\sum_r \ln\{1 + a\exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\}\} + \frac{1}{T}\sum_r \overline{n}_r(\epsilon_r + u'(\overline{n}) - \mu) \tag{15.23}$$

The mean energy follows from

$$\begin{aligned}
\overline{E} &= \left.\frac{\partial(\Phi\beta)}{\partial\beta}\right|_{z,V} \\
&= \left.\frac{\partial}{\partial\beta}(\beta V u(\overline{n}) - \beta\overline{N}u'(\overline{n}))\right|_{z,V} \\
&\quad - a\sum_r \frac{az\exp\{-\beta(\epsilon_r + u'(\overline{n}))\}}{1 + az\exp\{-\beta(\epsilon_r + u'(\overline{n}))\}}\left(-\epsilon_r - \left.\frac{\partial}{\partial\beta}(\beta u'(\overline{n}))\right|_{z,V}\right) \\
&= U(V,\overline{n}) + \beta V \left.\frac{\partial u(\overline{n})}{\partial\beta}\right|_{z,V} - \overline{N}\left.\frac{\partial(\beta u'(\overline{n}))}{\partial\beta}\right|_{z,V} - \beta u'(\overline{n})\left.\frac{\partial\overline{N}}{\partial\beta}\right|_{z,V} \\
&\quad + \sum_r \frac{\epsilon_r}{\exp\{\beta(\epsilon_r + u'(\overline{n}))\}z^{-1} + a} + \overline{N}\left.\frac{\partial(\beta u'(\overline{n}))}{\partial\beta}\right|_{z,V}
\end{aligned}$$

Due to

$$\left.\frac{\partial u(\overline{n})}{\partial\beta}\right|_{z,V} = u'(\overline{n})\left.\frac{\partial\overline{n}}{\partial\beta}\right|_{z,V} = \frac{1}{V}u'(\overline{n})\left.\frac{\partial\overline{N}}{\partial\beta}\right|_{z,V}$$

the second term cancels the fourth. It remains that

$$\overline{E} = \sum_r \overline{n}_r\epsilon_r + U(V,\overline{n}) = \sum_r \overline{n}_r\epsilon_r + Vu(\overline{n}) \tag{15.24}$$

as one would have expected according to Equation (15.9).

The role of the additional terms in Equation (15.18) is to cancel partial derivatives of $u'(\overline{n})$, which result from differentiating $\ln\{1 + a\exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\}\}$, so that the terms (15.21), (15.22), and (15.24) result, which are physically immediately plausible.

Before we calculate the pressure, we want to verify the validity of the derived relations in the thermodynamic limit. In the thermodynamic limit, $N \to \infty$, $V \to \infty$, $\frac{N}{V} = \text{const.}$, the mean particle number, entropy, and energy are *extensive* state quantities; i.e., all three are *proportional to the volume*. Due to the substitution

$$\sum_r \longrightarrow \frac{gV}{(2\pi)^3}\int d^3\vec{p}$$

in the thermodynamic limit (g is the degeneracy factor) this is valid only if $u'(\overline{n})$ *does not depend on the volume* (cf. Equations (15.21) and (15.23)), and *furthermore, if* $u(\overline{n})$ *does not depend on the volume* (cf. Equation (15.24)). This leads to the requirement that the particle number density $\overline{n} = \frac{\overline{N}}{V}$ must not depend on the volume. We check this as follows. We have

$$\left.\frac{\partial\overline{n}}{\partial V}\right|_{\mu,T} = \left.\frac{\partial}{\partial V}\left(\frac{\overline{N}}{V}\right)\right|_{\mu,T} = \frac{1}{V}\left(\left.\frac{\partial\overline{N}}{\partial V}\right|_{\mu,T} - \frac{\overline{N}}{V}\right)$$

Now,

$$\left.\frac{\partial \overline{N}}{\partial V}\right|_{\mu,T} = \frac{g}{(2\pi)^3}\int d^3\vec{p}\,\frac{1}{\exp\{\beta(\epsilon(p)+u'(\overline{n})-\mu)\}+a}$$

$$+\frac{gV}{(2\pi)^3}\int d^3\vec{p}\left(-\left(\frac{1}{\exp\{\beta(\epsilon(p)+u'(\overline{n})-\mu)\}+a}\right)^2\right)$$

$$\exp\{\beta(\epsilon(p)+u'(\overline{n})-\mu)\}\beta\left.\frac{\partial u'(\overline{n})}{\partial V}\right|_{\mu,T}$$

For the first term we write $\frac{\overline{N}}{V}$; the second we rewrite using $\left.\frac{\partial u'(\overline{n})}{\partial V}\right|_{\mu,T} = u''(\overline{n})\left.\frac{\partial \overline{n}}{\partial V}\right|_{\mu,T} = u''(\overline{n})\frac{1}{V}\left(\left.\frac{\partial \overline{N}}{\partial V}\right|_{\mu,T} - \frac{\overline{N}}{V}\right)$ as

$$-\sum_r \overline{n}_r^2\frac{\beta}{V}u''(\overline{n})\left(\left.\frac{\partial \overline{N}}{\partial V}\right|_{\mu,T} - \frac{\overline{N}}{V}\right)\exp\{\beta(\epsilon_r + u'(\overline{n}) - \mu)\}$$

Therefore, we have

$$\left.\frac{\partial \overline{n}}{\partial V}\right|_{\mu,T} = \frac{1}{V}\left(\left.\frac{\partial \overline{N}}{\partial V}\right|_{\mu,T} - \frac{\overline{N}}{V}\right)$$

$$= \frac{1}{V}\left(-\sum_r \overline{n}_r^2\frac{\beta}{V}u''(\overline{n})\exp\{\beta(\epsilon_r + u'(\overline{n}) - \mu)\}\right)\left(\left.\frac{\partial \overline{N}}{\partial V}\right|_{\mu,T} - \frac{\overline{N}}{V}\right)$$

This relation is true if

$$1 = -\sum_r \overline{n}_r^2\frac{\beta}{V}\exp\{\beta(\epsilon_r + u'(\overline{n}) - \mu)\}u''(\overline{n})$$

However, in general this is not the case, since $u(n)$ is at first a completely arbitrary interaction potential density. Thus it *must* hold that

$$\left.\frac{\partial \overline{N}}{\partial V}\right|_{\mu,T} = \frac{\overline{N}}{V} \tag{15.25}$$

i.e., $\left.\frac{\partial \overline{n}}{\partial V}\right|_{\mu,T}$ vanishes.

After these preliminary remarks we derive the pressure:

$$p = -\left.\frac{\partial \Phi}{\partial V}\right|_{\mu,T} = -u(\overline{n}) + u'(\overline{n})\left.\frac{\partial \overline{N}}{\partial V}\right|_{\mu,T}$$

$$+\frac{Ta}{V}\sum_r \ln\{1 + a\exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\}\}$$

$$= -\frac{\Phi}{V} \tag{15.26}$$

where we have used Equation (15.21) and the fact that the particle number density does not depend on the volume; consequently, $u(\overline{n})$ and $u'(\overline{n})$ are also independent of the volume. We

already derived the result (15.26) in the interaction-free case, when we inserted the Euler Equation (15.10) into the definition of $\Phi = \overline{E} - TS - \mu\overline{N}$. Consequently, Equation (15.10) is also fulfilled in the present case. However, one also can convince oneself of this fact via another argument, and show that $\Phi = -T \ln \mathcal{Z}$ is still defined as $\overline{E} - TS - \mu\overline{N}$, by using Equations (15.21), (15.23), and (15.24):

$$\begin{aligned}\overline{E} - TS - \mu\overline{N} &= \sum_r \overline{n}_r \epsilon_r + Vu(\overline{n}) - Ta \sum_r \ln\{1 + a \exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\}\} \\ &\quad - \sum_r \overline{n}_r (\epsilon_r + u'(\overline{n}) - \mu) - \mu \sum_r \overline{n}_r \\ &= Vu(\overline{n}) - u'(\overline{n})\overline{N} - Ta \sum_r \ln\{1 + a \exp\{-\beta(\epsilon_r + u'(\overline{n}) - \mu)\}\} \\ &= \Phi\end{aligned}$$

The Euler Equation (15.10) follows, using Equation (15.26).

Example 15.2: Phase transition between the quark–gluon plasma and the hadronic gas in heavy-ion collisions

The interacting quantum gas treated in the last Exercise is important, for example, for a thermodynamic description of the phase transition between a quark–gluon plasma (QGP) and hadronic matter in heavy-ion collisions.

In the last Example we saw that a simple criterion was the stability condition for the transition between a QGP and normal, neutral color, confined nuclear matter: if the bag pressure is larger than the pressure exerted by the gluons and quarks, the plasma is unstable and decays into separate quark bags, the nucleons. This very simple argument gives the order of magnitude of the quantities μ_c and T_c characterizing the phase transition. However, we have to take into account that the plasma is not suddenly created during the heavy-ion collision, but that it is formed out of highly compressed and strongly heated nuclear matter. Thus, we have a two-phase system during the transition. For a complete description of the system (assuming thermodynamic equilibrium), we have to apply Gibbs' phase coexistence relations,

$$T_{\mathrm{QGP}} = T_{\mathrm{Nuc}}$$

$$\mu_{\mathrm{QGP}} = \mu_{\mathrm{Nuc}}$$

$$p_{\mathrm{QGP}} = p_{\mathrm{Nuc}}$$

To this end, we need the equation of state of the QGP and of the hadronic phase. While the relations derived in the last Example for an ultrarelativistic gas of quarks and gluons can be used for the QGP, we assume the nucleonic phase to be a mixture of interacting quantum gases, consisting of nucleons and their resonances, and of mesons (cf. Volume 2 of this series). The interaction $U(V, n)$ is completely unrestricted in its functional form, except for the fact that one can write it as $Vu(n)$. In general, it is constructed in such a way that the total energy of nuclear matter has a minimum in the ground state (at $T = 0$, the measured ground state density $n_0 = 0.17\ \mathrm{fm}^{-3}$, the ground state binding energy $B_0 = -16$ MeV for infinite nuclear matter, and the ground state incompressibility $K \simeq 210$ MeV, determined from giant monopole resonances), namely, just the value B_0. For larger densities, $U(V, n)$ strongly increases to describe the repulsion of the nucleons.

The ansatz

$$U(V, n) = V\left(\frac{K}{18n_0}(n - n_0)^2 - B_0 n + f(n)\right)$$

is an example where the first part represents the *compressional energy* of nuclear matter. The second part $f(n)$ is needed to compensate the Fermi energy of the nucleons in the ground state, which is by definition contained in the compressional energy. The Fermi energy in the ground state enters already via the kinetic part of the total energy.

PART IV

REAL GASES AND PHASE TRANSITIONS

16 Real Gases

In the following section we will show how the properties of real gases whose constituents interact by virtue of a two-particle potential U_{ik} can be calculated approximately. The Hamiltonian reads

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \sum_{i,k,i<k} U_{ik}\,(|\vec{r}_i - \vec{r}_k|) \tag{16.1}$$

provided U_{ik} depends only on the distance $|\vec{r}_i - \vec{r}_k|$ between particles. Now the partition function

$$Z(T, V, N) = \frac{1}{N!h^{3N}} \int d^{3N}p \exp\left\{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^2\right\} \int d^{3N}r \exp\left\{-\beta \sum_{i,k,i<k} U_{ik}\right\} \tag{16.2}$$

has to be evaluated. The integrals over momenta do not cause difficulties:

$$\begin{aligned} Z(T, V, N) &= \frac{1}{N!h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \int d^{3N}r \exp\left\{-\beta \sum_{i,k,i<k} U_{ik}\right\} \\ &= \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \int d^{3N}r \prod_{i,k,i<k} \exp\{-\beta U_{ik}\} \end{aligned} \tag{16.3}$$

Yet to be evaluated is

$$Q_N(V, T) = \int d^{3N}r \prod_{i,k,i<k} \exp\{-\beta U_{ik}\} \tag{16.4}$$

If $U_{ik} = 0$, then $Q_N = V^N$, and we recover the result for an ideal gas.

In order to give an approximation for Z in the case $U_{ik} \neq 0$, let us consider the typical feature of the potential. It is strongly repulsive for very small distances and attractive for larger distances between particles. It vanishes at $r_{ik} \to \infty$. Given low densities of the gas, the mean distance between two particles is very large, so that the gas approximately

behaves like an ideal gas. The same is valid for high temperatures, because then the mean potential energy of the particles is small compared with their mean kinetic energy kT.

Therefore it is sensible to expand Z around the limiting case of the ideal gas. Now if $\beta U_{ik} \ll 1$, then $\exp\{-\beta U_{ik}\} \approx 1$, and hence

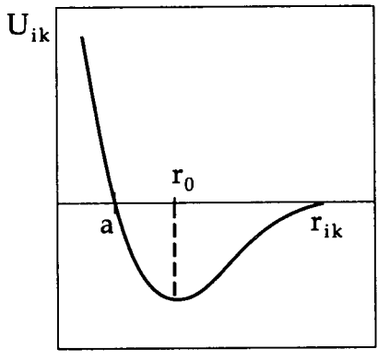


Figure 16.1.

$$f_{ik} = (\exp\{-\beta U_{ik}\} - 1) \qquad f_{ik} \ll 1 \tag{16.5}$$

is an appropriate parameter for this expansion, as $f_{ik} \to 0$ for $\langle r_{ik} \rangle \to \infty$ or $T \to \infty$. Now the following product has to be calculated:

$$\prod_{i,k,i<k} (1 + f_{ik}) = 1 + \sum_{i,k,i<k} f_{ik} + \sum_{i,k,l,m} f_{ik} f_{lm} + \cdots \tag{16.6}$$

In the next section higher orders of the series (16.6) will be investigated in more detail. Here we restrict our considerations to the first two terms. Inserting Equation (16.6) into (16.4) yields

$$\begin{aligned} Q_N(V, T) &= \int d^{3N}r \left(1 + \sum_{i,k,i<k} f_{ik} + \cdots\right) \\ &= V^N + V^{N-2} \sum_{i,k,i<k} \int d^3 r_i \int d^3 r_k \, (\exp\{-\beta U_{ik}\} - 1) \\ &\quad + \cdots \end{aligned} \tag{16.7}$$

The leading term V^N is identical with the result for Q_N in the case of an ideal gas. The following terms represent corrections due to the interaction U_{ik}. Substituting center-of-mass coordinates $\vec{R} = \frac{1}{2}(\vec{r}_i + \vec{r}_k)$ and relative coordinates $\vec{r} = (\vec{r}_i - \vec{r}_k)$ in the integral leads to

$$Q_N(V, T) = V^N + V^{N-1} \frac{N(N-1)}{2} \int d^3 r \, (\exp\{-\beta U(r)\} - 1) + \cdots \tag{16.8}$$

for there are $N(N-1)/2$ pairs with $i < k$ which all give the same contribution to Z. Defining

$$a(T) = \int d^3 r \, (\exp\{-\beta U(r)\} - 1) = 4\pi \int_0^\infty r^2 \, dr \, (\exp\{-\beta U(r)\} - 1) \tag{16.9}$$

we get from Equation (16.3), with $N \gg 1$, $N(N-1)/2 \approx N^2/2$,

$$\begin{aligned} Z(T, V, N) &= \frac{1}{N!} \left(\frac{2\pi m k T}{h^2}\right)^{3N/2} \left[V^N + V^{N-1} \frac{N^2}{2} a(T) + \cdots\right] \\ &= \frac{1}{N!} \frac{V^N}{\lambda^{3N}} \left[1 + \frac{N^2 a(T)}{2V} + \cdots\right] \end{aligned} \tag{16.10}$$

The thermal equation of state of the gas can now be calculated from the free energy:

$$p(T, V, N) = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{\partial}{\partial V}(kT \ln Z) = \frac{NkT}{V} - kT\frac{\frac{a}{2}\frac{N^2}{V^2}}{1 + \frac{a}{2}\frac{N^2}{V}} \tag{16.11}$$

$$p \approx \frac{NkT}{V}\left(1 - \frac{a}{2}\frac{N}{V}\right) \tag{16.12}$$

Here we have considered only the two leading terms in Equation (16.10), and in Equation (16.12) we have made use of the fact that $a(T)$ is just a small correction.

Example 16.1: The Sutherland potential

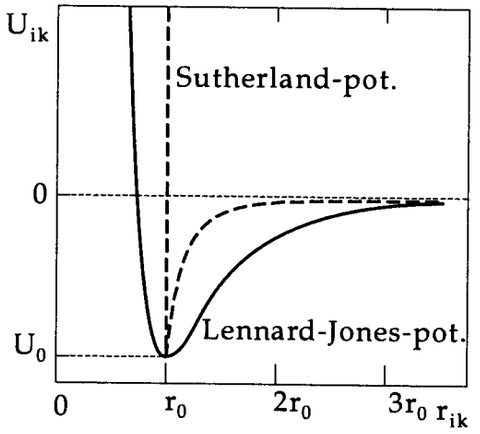


Figure 16.2. Sutherland and Lennard–Jones potential.

The equation of state (16.12) shall be evaluated for a realistic case. For this purpose the interaction potential $U(r)$ of the particles must be given, e.g., the *Lennard–Jones potential*, also called the 12/6-potential,

$$U(r) = U_0\left(\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^6\right)$$

This potential possesses a minimum at $r = r_0$ with the depth $-U_0$, and a strongly repulsive part for small r. Although it is quite realistic we do not discuss this potential here, as the evaluation of Equation (16.9) is very tiresome. We better employ the *Sutherland potential*,

$$U(r) = \begin{cases} +\infty & r < r_0 \\ -U_0\left(\frac{r_0}{r}\right)^6 & r \geq r_0 \end{cases}$$

Here the atoms are regarded as solid spheres with radii $r_0/2$. (r denotes the relative distance $|\vec{r}_i - \vec{r}_k|$. The minimum distance r_0 between solid spheres is just twice the radius of one sphere.) For $r > r_0$, the potential is attractive and proportional to r^{-6}. Herewith Equation (16.9) reads

$$a(T) = 4\pi\int_0^{r_0} r^2\,dr(-1) + 4\pi\int_{r_0}^{\infty} r^2\,dr\left(\exp\left\{\beta U_0\left(\frac{r_0}{r}\right)^6\right\} - 1\right)$$

As per our assumption, we have $\beta U_0 \ll 1$, and hence

$$\exp\left\{\beta U_0\left(\frac{r_0}{r}\right)^6\right\} \approx 1 + \beta U_0\left(\frac{r_0}{r}\right)^6 + \cdots$$

$$a(T) \approx -\frac{4\pi}{3}r_0^3 + 4\pi\beta U_0\int_{r_0}^{\infty} r^2\,dr\left(\frac{r_0}{r}\right)^6$$

$$\approx -\frac{4\pi}{3}r_0^3(1 - \beta U_0)$$

Using this expression we obtain

$$p = \frac{NkT}{V}\left\{1 + \frac{2\pi r_0^3}{3v}\left(1 - \frac{U_0}{kT}\right)\right\}$$

with $v = V/N$. Alternatively,

$$\left(p + \frac{2\pi r_0^3 U_0}{3v^2}\right) = \frac{kT}{v}\left(1 + \frac{2\pi r_0^3}{3v}\right) \approx \frac{kT}{v}\left(1 - \frac{2\pi r_0^3}{3v}\right)^{-1} \tag{16.13}$$

In this last approximation we have used the fact that the proper volume $4\pi r_0^3/3$ of the atoms is small compared to the volume per particle v, provided the density is not too high (rarefied gas). As we can see, Equation (16.13) exactly corresponds to the van der Waals equation of state

$$\left(p + \frac{a}{v^2}\right)(v - b) = kT$$

and we have thus microscopicly calculated the van der Waals parameters a and b (do not mix up this a with that in Equation (16.9)!):

$$a = \frac{2\pi}{3} r_0^3 U_0$$

$$b = \frac{2\pi}{3} r_0^3$$

The parameter a depends on the depth U_0 of the potential and measures the strength of the attractive force between particles, whereas b is the so-called covolume. The latter is not exactly identical with the volume of the particles because their minimum distance is r_0 and not $r_0/2$, which is the radius.

For absorption: Mayer's cluster expansion

The partition function of a real gas was derived at the beginning of this chapter:

$$Z(T, V, N) = \frac{1}{N!\lambda^{3N}} Q_N(V, T) \tag{16.14}$$

with

$$Q_N(V, T) = \int d^{3N}r \prod_{i,k,i<k}^{N} \exp\{-\beta U_{ik}\} = \int d^{3N}r \prod_{i,k,i<k}^{N} (1 + f_{ik}) \tag{16.15}$$

The product in the last expression can be calculated in a general fashion. There are exactly p=$\frac{1}{2}N(N-1)$ factors $(1 + f_{ik})$ (number of pairs (i,k) with $i < k$). Of course, the leading term is just $1^p = 1$. The second term can be obtained by replacing one of the p factors by a factor f_{ik} and summing over all possible combinations. Correspondingly, in the third term there are two factors f_{ik}, etc.:

$$\prod_{i,k,i<k}^{N} (1 + f_{ik}) = 1 + \sum_{i,k,i<k} f_{ik} + \sum_{i_1,i_2,k_1,k_2}{}' f_{i_1k_1} f_{i_2k_2} + \sum_{i_1,\ldots,i_p,k_1,\ldots,k_p}{}' f_{i_1k_1} \cdots f_{i_pk_p} \tag{16.16}$$

The primes attached to the sums indicate that the indices have to satisfy certain conditions. Of course, we must have $i_1 < k_1$, $i_2 < k_2, \ldots, i_p < k_p$. However, there is one more condition which can easily be understood by ordering the factors $(1 + f_{ik})$ according to the pairs

(i, k). For this purpose one relates a number between 1 and p to every pair (i, k) in a definite way; let us call this number $\text{num}(i, k)$ (especially easy to survey is the so-called lexicographic order: pairs are first arranged according to their first index and then, given the same first index, according to the second index). Now if one reorders the factors on the left-hand side of Equation (16.16) with respect to their (increasing) numbers, $\text{num}(i, k)$, and preserves this order when multiplying out, then the factors $f_{i_1k_1}, f_{i_2k_2}, \ldots$ in the sums on the right-hand side also must display increasing numbers of the pairs $(i_1, k_1), (i_2, k_2), \ldots$, respectively. Hence the second condition imposed on the sums is $\text{num}(i_1, k_1) < \text{num}(i_2, k_2) < \cdots$. This implies that the last sum in Equation (16.16) contains only a single term, for there is only one possibility if all p pairs occur and have to be sorted according to their numbers.

Thus we now have to calculate

$$Q_N(V, T) = \int d^{3N}r \left(1 + \sum_{i,k,i<k} f_{ik} + \sum_{i_1,i_2,k_1,k_2}{}' f_{i_1k_1} f_{i_2k_2} + \sum_{i_1,\ldots,i_p,k_1,\ldots,k_p}{}' f_{i_1k_1} \cdots f_{i_pk_p}\right) \tag{16.17}$$

This seems to be impossible in the general case. However, one immediately realizes that Equation (16.17) contains a lot of terms in the integrand which contribute the same value to the integral, e.g.,

$$\int d^{3N}r[\cdots f_{12} + f_{24} + \cdots] = \int d^{3N}r[\cdots 2f_{12} \cdots] \tag{16.18}$$

as integration variables may be arbitrarily renumbered. Furthermore, one recognizes a possibility of systematically decomposing and rearranging the terms in Equation (16.17) according to the following example: let $N = 14$ and

$$I = \int d^3r_1 \cdots d^3r_{14} f_{12} f_{14} f_{67} f_{89} f_{9,11} f_{12,13} \tag{16.19}$$

be a term in Equation (16.17). Obviously, Equation (16.19) can be rearranged:

$$I = \int d^3r_8 d^3r_9 d^3r_{11} f_{89} f_{9,11} \int d^3r_1 d^3r_2 d^3r_4 f_{12} f_{14} \int d^3r_6 d^3r_7 f_{67} \times \int d^3r_{12} d^3r_{13} f_{12,13} \int d^3r_3 \int d^3r_5 \int d^3r_{10} \int d^3r_{14} \tag{16.20}$$

i.e., Equation (16.19) can be decomposed into two factors, which represent integrals over the coordinates of two or three interacting particles, respectively, and some trivial integrals over a particle coordinate.

Because of the possibility of renumbering integration variables, which we pointed out in Equation (16.18), all factors with the same number of integrations over coordinates, namely the first two terms, the third and fourth terms, and the last four terms, of Equation (16.20), respectively, have the same value.

However, this cannot be generalized. For instance, in Equation (16.19) an additional factor $f_{8,11}$ might have occurred, which we then would have had to write in the integrand

of the first integral in Equation (16.20). Although the first two factors in Equation (16.20) would have been integrals over the same number of coordinates, their values would have been completely different, for in one case the integrand would have been a product of only two f_{ik}s, in the other case, however, a product of three.

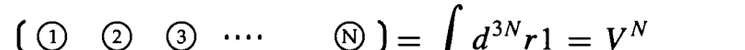
Of course, for large values of N and expressions with a structure even more complicated than the one of Equation (16.19), there may be more factors which represent integrals over one, two, three, or more particle coordinates. Obviously, the most complicated terms in Equation (16.17) are those which cannot be decomposed into factors, i.e., those which contain products of f_{ik}s where i or k take on all allowed values between 1 and N.

After these introductory remarks, we see that many terms in Equation (16.17) have the same value, and at least some have common structures. Hence one can suppose that it will not be necessary to evaluate all the terms in Equation (16.17), one by one, but only certain representatives of classes. Then one just has to count all the members of a class.

The method we are going to introduce in the following was developed in 1937 by Mayer and his collaborators. It will become particularly clear if we represent the terms in Equation (16.17) graphically. We relate every term in Equation (16.17) to an N-particle graph by representing the N particles by numbered circles and every factor f_{ik} by a line between the particles i and k. The way in which the circles and lines are arranged is of no importance. They may be arbitrarily shifted with respect to each other so that the graph becomes as easy to survey as possible. Therefore, lines may cross. Two N-particle graphs are to be regarded as identical if they can be transformed into each other by shifting particles together with all the lines connected with these particles. Thus Equation (16.17) can also be interpreted in the following way:

$$Q_N(V, T) = \text{Sum of all different } N\text{-particle graphs} \tag{16.21}$$

The first term in Equation (16.17) is, according to this prescription, a graph without any line



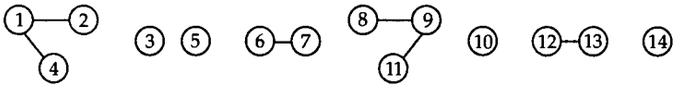
$$= \int d^{3N}r1 = V^N \tag{16.22}$$

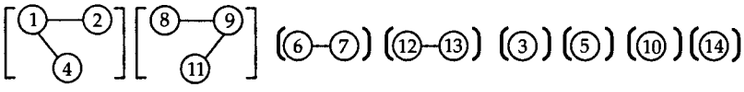
In the second term, a sum of all graphs appears, in which exactly one particle is connected with another, e.g.,

$$= \int d^{3N}r f_{12}$$

$$= \int d^{3N}r f_{24} \tag{16.23}$$

As already mentioned, all these summands have the same value. Quite analogously, we can also represent expression (16.19) for $N = 14$ by a 14-particle graph:

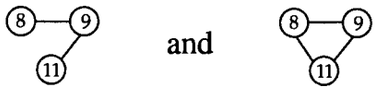
$I =$ 

$=$ 

$$\tag{16.24}$$

where we have reordered the circles in the last line and put the connected parts of the graph in square brackets. Obviously each factor in Equation (16.20) corresponds to a square bracket in Equation (16.24). One calls the connected parts of the graph a *cluster*. Hence, two 3-particle clusters, or simply 3-clusters, two 2-clusters and four 1-clusters occurs in Equation (16.24).

As mentioned above, the two 3-clusters have the same value in this example, as well as the two 2-clusters and the four 1-clusters. That this is not always the case for clusters with 3 or more particles, we have already made clear. One can readily understand this graphically, e.g., the 3-clusters



(16.25)

have different values due to the additional link (interaction) between particles 8 and 11 (the additional factor $f_{8,11}$) in the second cluster in Equation (16.25).

Each N-particle graph can be factored into such clusters. There are, however, also N-particle graphs, which consist of a single cluster (N-cluster). Thus, we can construct an arbitrary graph of such clusters. In general, such a graph will contain m_1 1-clusters, m_2 2-clusters, ..., m_N N-clusters. For the 14-particle graph (16.24), for instance, $m_1 = 4, m_2 = 2, m_3 = 2, m_4 = m_5 = \cdots = m_{14} = 0$. The numbers m_l have to fulfill the condition

$$\sum_{l=1}^{N} m_l l = N \tag{16.26}$$

since the sum of all particles in the particular clusters is just equal to the total particle number.

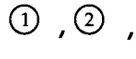
Each N-particle graph can now be classified by fixing the set $\{m_1, \ldots, m_N\}$. The sum of all N-particle graphs which belong to a fixed set $\{m_1, \ldots, m_N\}$ will be denoted by $S\{m_1, \ldots, m_N\}$. If we now perform the sum of all $S\{m_1, \ldots, m_N\}$ over all possible sets $\{m_1, \ldots, m_N\}$, which fulfill condition (16.26), we will register all possible N-particle graphs; i.e., Equations (16.17) or (16.22) can be written as

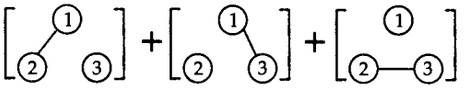
$$Q_N(V, T) = \sum_{\{m_1,\ldots,m_N\}}{}' S\{m_1, \ldots, m_N\} \tag{16.27}$$

where the prime on the sum indicates that condition (16.26) has to be fulfilled in the summation. For 3 particles, Equation (16.27) reads, for example,

$$Q_3(V, T) = S\{3, 0, 0\} + S\{1, 1, 0\} + S\{0, 0, 1\} \tag{16.28}$$

since for $N = 3$ only three sets $\{m_1, m_2, m_3\}$ fulfill condition (16.26). The corresponding graphs are

$S\{3, 0, 0\} =$ 

$S\{1, 1, 0\} =$ 

$$S\{0, 0, 1\} = \left[\begin{array}{c}1\\2\quad 3\end{array}\right] + \left[\begin{array}{c}1\\2\text{—}3\end{array}\right] + \left[\begin{array}{c}1\\2\text{—}3\end{array}\right] + \left[\begin{array}{c}1\\2\text{—}3\end{array}\right] \tag{16.29}$$

Due to Equation (16.27), our problem now reduces to the determination of the sums $S\{m_1, \ldots, m_N\}$ for fixed numbers $\{m_1, \ldots, m_N\}$.

The numbers $m_1, \ldots, m_N$ determine how many 1-clusters, 2-clusters, ..., N-clusters are contained in an N-particle graph. Thus, in $S\{m_1, \ldots, m_N\}$ *all* graphs are contained, with m_1 1-clusters, ..., m_N N-clusters. The structure of all these graphs is identical inasmuch as for each graph there exist m_1 single circles, 2 m_2 circles connected by a line to form a 2-cluster, 3 m_3 circles connected by two or three lines to form a 3-cluster, etc. Obviously, there are several different types of l-cluster with a certain particle number l, for instance the two 3-clusters in Equation (16.25) (we will soon precisely define what we mean by the word *type*). It is essential to understand that the set $\{m_1, \ldots, m_N\}$ does not fix the numbering of the circles. If we consider a graph of $S\{m_1, \ldots, m_N\}$ with a certain structure of circles and links, and a fixed numbering of circles, we can also find graphs in $S\{m_1, \ldots, m_N\}$ which originate from the first via a permutation of the particle numbers. However, not every permutation leads to a new graph (see, e.g., the second graph in Equation (16.25). There one can permutate the particle numbers 8,9, and 11 without obtaining a new graph; a new graph can only be obtained if a new particle number appears). Of course, in $S\{m_1, \ldots, m_N\}$ all graphs also appear which contain different types of clusters and which cannot be transformed into each other by a permutation of the particle numbers.

The structure of the terms in $S\{m_1, \ldots, m_N\}$ is always the same. Each term of the sum factors according to

$$\text{Term in } S\{m_1, \ldots, m_N\} = [m_1 \text{ 1-cluster}] \cdots [m_N N\text{-cluster}] \tag{16.30}$$

Hence, if all m_l l-clusters have the same value, an N-particle graph characterized by Equation (16.30) could be written as $\prod_{l=1}^{N} (l\text{-cluster})^{m_l}$. However, this is not correct, since the different types of l-clusters may have different values. At this point, we have to specify what we mean by a *type of cluster*. To this end, it is sufficient to define when two clusters of equal particle number are of the same type. First of all, the two clusters which are to be compared do not necessarily have to contain the same particle numbers. Since the value of a cluster does not change by a simple renumbering, we may change the particle numbers in a cluster, such that they coincide with the numbers of the other cluster. However, the order of the numbers is not to be changed. For instance, if one 3-cluster contains the numbers 1,2,3 and the other the numbers 8,9,11, we have to renumber 8,9,11 to 1,2,3 or 1,2,3 to 8,9,11; other ways of renumbering would change the order. If both clusters contain the same particle numbers they can be directly compared. They are identical (i.e., of the same type), if they can be transformed into each other by a shift of the particles with the respective links. Here also, the particle numbers have to coincide. According to this rule, the two 3-clusters in Equation (16.25) are of different types, 3-clusters of the same type would be

$$\left[\begin{array}{c}1\text{—}2\\3\end{array}\right] \qquad \left[\begin{array}{c}8\text{—}9\\11\end{array}\right] \tag{16.31}$$

In the lowest line of Equation (16.29), the four possible types of 3-clusters are shown. They cannot be transformed into each other via shifts. An arbitrary 3-cluster with other particle numbers is uniquely mapped onto one of these types by our definition.

Trivially, there is only one type of 1-cluster and only one type of 2-cluster, but there are four different types of 3-clusters, etc. Different types of l-clusters do not necessarily have different values. For instance, all graphs of l-clusters, which originate from a permutation of the particles, have the same value (e.g., the first three 3-cluster in the last line of Equation (16.29)).

Let there be K_l different types of l-clusters. Then each factor in Equation (16.30) can be classified according to these types. The m_l l-cluster can consist of n_1 l-clusters of type 1, n_2 l-clusters of type 2, ..., n_{K_l} l-clusters of type K_l:

$$[m_l l\text{-cluster}] = [n_1 l\text{-cluster of type 1}][n_2 l\text{-cluster of type 2}] \cdots [n_{K_l} l\text{-cluster of type } K_l] \tag{16.32}$$

The numbers $n_1, \ldots, n_{K_l}$ have to fulfill the condition

$$\sum_{i=1}^{K_l} n_i = m_l \tag{16.33}$$

since there will be exactly m_l l-clusters. For instance, the 14-particle graph (16.24) decomposes into the factors

[2 3-clusters][2 2-clusters][4 1-clusters] (16.34)

according to Equation (16.30), and the first of these factors can be written as

[2 3-clusters] = [1 3-cluster of type 1][1 3-cluster of type 2] (16.35)

where the enumeration of the types is, of course, arbitrary. Since all l-clusters of a certain type have the same value, Equation (16.32) is identical to

$$[m_l l\text{-cluster}] = [\text{type } 1]^{n_1} [\text{type } 2]^{n_2} \cdots [\text{type } K_l]^{n_{K_l}} \tag{16.36}$$

Now we have decomposed each N-particle graph which contributes to $S\{m_1, \ldots, m_N\}$ into its smallest (not further reducible) parts. We still have to summarize the terms in the sum.

Let us first consider all terms of $S\{m_1, \ldots, m_N\}$, where all partial graphs (factors) are fixed (including particle numbers, positions of the links, etc.) except for the factor [m_l l-cluster], which will run over all possible partial graphs. All the terms in the sum possess the same factors [m_1 1-clusters] $\cdots$ [m_{l-1} $(l-1)$-clusters][m_{l+1} $(l+1)$-clusters] $\cdots$ [m_N N-clusters], and differ only by the factor [m_l l-clusters].

The particle numbers contained in the m_l l-clusters are fixed, since the particle numbers in the fixed factors are not to be changed. However, the m_l l-clusters in each term of the sum can be composed of quite different types of l-clusters, and the available lm_l particles can be distributed among the cluster types in different ways.

The set of these terms is still rather complex. Therefore, we first consider a subset of all terms under consideration, namely those in which each l-cluster is formed of fixed particle numbers. Since now the particle numbers are fixed in each m_l l-cluster, *two graphs*

under consideration can differ only in their composition of particular l-cluster types; i.e., if they have different sets of numbers $\{n_1, \ldots, n_{K_l}\}$ which have to fulfill condition (16.33). Therefore, one runs through all terms of the considered subset if one sums over these sets of numbers. The factor [m_l l-clusters] belonging to this subset of graphs thus reads

$$[m_l l\text{-cluster}] = \sum_{\substack{n_1, \ldots, n_{K_l} = 0 \\ n_1 + \cdots + n_{K_l} = m_l}}^{m_l} [\text{type } 1]^{n_1} [\text{type } 2]^{n_2} \cdots [\text{type } K_l]^{n_{K_l}} \tag{16.37}$$

An analogous consideration can be performed for each l. Thus, we obtain for the sum of all different N-particle graphs which contribute to $S\{m_1, \ldots, m_N\}$ and where the numbers of the particles which form the particular clusters are fixed:

$$[m_l l\text{-cluster}]$$

$$= \prod_{l=1}^{N} \left(\sum_{\substack{n_1, \ldots, n_{K_l} = 0 \\ n_1 + \cdots + n_{K_l} = m_l}}^{m_l} [\text{type } 1]^{n_1} [\text{type } 2]^{n_2} \cdots [\text{type } K_l]^{n_{K_l}} \right) \tag{16.38}$$

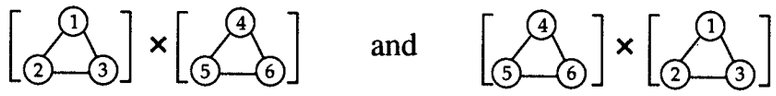
Note that permutations of the particle numbers *inside* a cluster are implicitly contained in Equation (16.38). Such permutations either lead, as we have already seen, to another type of cluster and thus to another set of numbers $n_1, \ldots, n_{K_l}$, or they do not change the cluster type, but then we do not have a different N-particle graph.

We now have to take into account that graphs also contribute to $S\{m_1, \ldots, m_N\}$ which belong to other distributions of the particle numbers over the respective clusters. These have not been considered up to now. Further types of graphs do not exist, since all different graphs which can be formed with given particle numbers for the clusters are contained in Equation (16.38). All graphs not considered up to now originate from those already considered, via permutations of the particle numbers. Since such permutations correspond to a renumbering of the integration variables, and since therefore all these graphs have the same value, we need only multiply Equation (16.38) by the correct factor. There are in total $N!$ permutations of the particle numbers. However, permutations inside an l-cluster are not to be counted, since they are already contained in Equation (16.38). Thus, the factor should be

$$w\{m_1, \ldots, m_N\} = \frac{N!}{\prod_{l=1}^{N} (l!)^{m_l}} \tag{16.39}$$

This however, is, not quite correct. With this factor we would also count such permutations of the particle numbers which exchange only all particles of two l-clusters of the same type. Such an exchange does not correspond to a new graph but only to a rearrangement of two

factors, as one readily observes for the example of two 3-clusters of the same type:



(16.40)

There are exactly $n_j!$ possible permutations of all l-clusters of type j. The general factor [m_l l-clusters] thus contain $n_1!n_2!\cdots n_{K_l}!$ of such rearrangements for a given set of numbers $n_1 \cdots n_{K_l}$. If we want to use the factor (16.39), we have to divide the sum in (16.38) by the factor $n_1!n_2!\cdots n_{K_l}!$. The final result thus reads

$$S\{m_1, \ldots, m_N\} =$$

$$N! \prod_{l=1}^{N} \frac{1}{(l!)^{m_l}} \left(\sum_{n_1,\ldots,n_{K_l}=0 n_1+\cdots+n_{K_l}=m_l}^{m_l} \frac{[\text{type } 1]^{n_1}}{n_1!} \frac{[\text{type } 2]^{n_2}}{n_2!} \cdots \frac{[\text{type } K_l]^{n_{K_l}}}{n_{K_l}!} \right) \tag{16.41}$$

This equation can be simplified using the polynomial theorem:

$$\sum_{n_1,\ldots,n_{K_l}=0 n_1+\cdots+n_{K_l}=m_l}^{m_l} \frac{1}{n_1! \cdots n_{K_l}!} [\text{type } 1]^{n_1} \cdots [\text{type } K_l]^{n_{K_l}}$$

$$= \frac{1}{m_l!} (\text{type } 1 + \text{type } 2 + \cdots + \text{type } K_l)^{m_l} \tag{16.42}$$

In other words: the sum $S\{m_l\}$ can be expressed as the sum of all types of l-clusters with fixed particle numbers:

$$S\{m_1, \ldots, m_N\} = N! \prod_{l=1}^{N} \frac{1}{(l!)^{m_l} m_l!} (\text{Sum of all types of } l\text{–clusters})^{m_l} \tag{16.43}$$

The main simplification we have achieved is that now one has only to evaluate the integrals for the single cluster types with a fixed enumeration of the particles, and no longer for the full N-particle graphs. We now define the abbreviation

$$b_l(V, T) = \frac{1}{l!\lambda^{3(l-1)}V} (\text{Sum of all types of } l\text{-clusters}) \tag{16.44}$$

We will interpret these dimensionless numbers (16.44) later on. The factor $l!^{-1}$ for each l-cluster results from the corresponding prefactor in Equation (16.43). The prefactor $\lambda^{-3(l-1)}V^{-1}$ renders the expression dimensionsless and affords us a way to express Equation (16.43) in terms of the b_l which is as simple as possible:

$$S\{m_1, \ldots, m_N\} = N!\lambda^{3N} \prod_{l=1}^{N} \frac{1}{m_l!} \left(b_l \frac{V}{\lambda^3} \right)^{m_l} \tag{16.45}$$

The factor $Q_N(V, T)$ in the canonical partition function is therefore

$$Q_N(V, T) = N!\lambda^{3N} \sum_{\{m_1,\ldots,m_N\}}{}' \prod_{l=1}^{N} \frac{1}{m_l!} \left(b_l \frac{V}{\lambda^3} \right)^{m_l} \tag{16.46}$$

The canonical partition function now reads

$$Z(T, V, N) = \sum_{\{m_1,\ldots,m_N\}}{}' \prod_{l=1}^{N} \frac{1}{m_l!} \left(b_l \frac{V}{\lambda^3} \right)^{m_l} \tag{16.47}$$

where the prime on the sum indicates that one has to sum only over such sets $\{m_1, \ldots, \}$ which fulfill condition (16.26). This somewhat inconvenient condition vanishes, if we consider the grand canonical partition function

$$\mathcal{Z}(T, V, z) = \sum_{N=0}^{\infty} z^N Z(T, V, N) \tag{16.48}$$

One writes

$$z^N = z^{\sum_l l m_l} = \prod_{l=1}^{N} (z^l)^{m_l} \tag{16.49}$$

and it follows that

$$\mathcal{Z}(T, V, N) = \sum_{N=0}^{\infty} \sum_{\{m_1,\ldots,m_N\}}{}' \prod_{l=1}^{\infty} \frac{1}{m_l!} \left(b_l z^l \frac{V}{\lambda^3} \right)^{m_l} \tag{16.50}$$

Here the second sum is still restricted by the constraint $\sum_l m_l = N$. However, since one also sums over all particle numbers N, this is equivalent to

$$\begin{aligned} \mathcal{Z}(T, V, N) &= \sum_{m_1,m_2,\ldots,=0}^{\infty} \prod_{l=1}^{\infty} \frac{1}{m_l!} \left(b_l z^l \frac{V}{\lambda^3} \right)^{m_l} \\ &= \prod_{l=1}^{\infty} \left[\sum_{m_l=0}^{\infty} \frac{1}{m_l!} \left(b_l z^l \frac{V}{\lambda^3} \right)^{m_l} \right] \\ &= \prod_{l=1}^{\infty} \exp\left\{ b_l z^l \frac{V}{\lambda^3} \right\} = \exp\left\{ \frac{V}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l \right\} \end{aligned} \tag{16.51}$$

Therewith the grand canonical potential can be immediately calculated:

$$\phi = -kT \ln \mathcal{Z} = -kT \frac{V}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l \tag{16.52}$$

Now we will take a closer look at the b_l and the meaning of the prefactor in Equation (16.44). To this end, we explicitly denote the b_l for the smallest cluster $l = 1, 2$:

$$b_1 = \frac{1}{V}(①) = \frac{1}{V} \int d^3 r_1 = 1 \tag{16.53}$$

$$\begin{aligned} b_2 &= \frac{1}{2\lambda^3 V}(①–②) = \frac{1}{2\lambda^3 V} \int d^3 r_1 \, d^3 r_2 f_{12} \\ &= \frac{1}{2\lambda^3} \int d^3 r_{12} f_{12} = \frac{2\pi}{\lambda^3} \int_0^{\infty} f(r) r^2 \, dr \end{aligned}$$

$$= \frac{2\pi}{\lambda^3} \int_0^\infty \left(\exp\left\{ -\frac{U(r)}{kT} \right\} - 1 \right) r^2 \, dr \tag{16.54}$$

Here the new coordinates $\vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2)$ and $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$ were substituted in the cluster integral to be calculated. The integration over the center-of-mass coordinates $\vec{R}$ of the cluster simply yields a factor V. An analogous substitution $\vec{R} = \frac{1}{l}(\vec{r}_1 + \cdots \vec{r}_l)$ is possible for all l-clusters, and always produces the same factor V. Therefore it is sensible to multiply all cluster integrals by $1/V$. After separating the center-of-mass part, the cluster integrals no longer depend on the volume (if it is large enough), but only on the range of the potential (as long as this is much smaller than the size of the container). The integrands decrease exponentially with the distance between the particles, so that one may extend the integration over the relative coordinates to infinite distances without error. Thus, we have

$$\lim_{V \to \infty} b_l(V, T) = b_l(T) \tag{16.55}$$

For b_3 one has four contributions from the different types of 3-clusters,

$$b_3 = \frac{1}{6\lambda^6 V} \left[\begin{array}{c} 1 \\ 2 \quad 3 \end{array} \right] + \left[\begin{array}{c} 1 \\ 2 - 3 \end{array} \right] + \left[\begin{array}{c} 1 \\ 2 - 3 \end{array} \right] + \left[\begin{array}{c} 1 \\ 2 - 3 \end{array} \right]$$

$$= \frac{1}{6\lambda^6 V} \int d^3r_1 \, d^3r_2 \, d^3r_3 \, [f_{12}f_{13} + f_{13}f_{23} + f_{12}f_{23} + f_{12}f_{13}f_{23}] \tag{16.56}$$

We have already found that the first three terms have the same value, since one can arbitrarily rename the integration variables and exploit $f_{ik} = f_{ki}$. If one finally substitutes $\vec{R} = \frac{1}{3}(\vec{r}_1 + \vec{r}_2 + \vec{r}_3)$ and $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, one has

$$b_3 = \frac{1}{6\lambda^6 V} \left[3V \int d^3r_{12} f_{12} \int d^3r_{13} f_{13} + V \int d^3r_{12} \, d^3r_{13} f_{12} f_{13} f_{23} \right]$$

$$= 2b_2^2 + \frac{1}{6\lambda^6} \int d^3r_{12} \, d^3r_{13} f_{12} f_{13} f_{23} \tag{16.57}$$

The first integral in Equation (16.57) factors and may therefore be expressed by the coefficient b_2, which is already evaluated. It is actually not necessary to calculate all l-clusters anew, but only certain types. One calls these types *irreducible l-clusters*.

The $b_l(V, T)$ are dimensionless numbers which do not depend on the volume in the thermodynamic limit, but only on the temperature, and which can be easily calculated successively. All thermodynamic properties of a real gas can now be determined by the cluster integrals $b_l(T)$. It is often sufficient to consider only the smallest cluster: for low gas densities the fugacity $z = \exp\{\mu/kT\}$ is also small ($z \ll 1$). The contribution of larger clusters can therefore be neglected. Furthermore, for low densities it is very improbable that many particles form a larger l-cluster. However, this does not hold near phase transitions. In this case many particles can form larger drops. Hence, many terms have to be explicitly calculated near phase transitions. From Equation (16.52) we directly obtain for the pressure of the real gas

$$\frac{p}{kT} = \frac{1}{V} \ln \mathcal{Z} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l \tag{16.58}$$

If one fixes the particle density of the gas instead of the chemical potential (or z), one has to determine z from condition (9.64):

$$\frac{N}{V} = \frac{kT}{V}\left.\frac{\partial}{\partial\mu}\ln\mathcal{Z}\right|_{T,V} = \frac{z}{V}\left.\frac{\partial}{\partial z}\ln\mathcal{Z}\right|_{T,V} = \frac{1}{\lambda^3}\sum_{l=1}^{\infty} l b_l z^l \tag{16.59}$$

Equations (16.58) and (16.59) are the famous *cluster expansions* of Mayer (1937).

Virial expansion

Equations (16.58) and (16.59) contain implicitly the thermal equation of state of the real gas; however, it is very convenient to look for an explicit expansion of this equation of state which corresponds to the phenomenological virial expansion presented in the thermodynamics part of this book. To this end, one has to eliminate the fugacity z from Equations (16.58) and (16.59). From Equation (16.59) one sees that z can depend only on the parameter $N\lambda^3/V$. Hence, there exists a series expansion

$$z = \sum_{l=1}^{\infty} c_l \left(\frac{\lambda^3}{v}\right)^l \tag{16.60}$$

with $v = V/N$. The coefficients c_l can depend only on the b_l. If one inserts Equation (16.60) into (16.58), one obtains, after ordering the powers of λ^3/v, a series expansion of the equation of state which is analogous to Equation (16.52), the *virial expansion*

$$\frac{pV}{NkT} = \sum_{l=1}^{\infty} a_l \left(\frac{\lambda^3}{v}\right)^{l-1} \tag{16.61}$$

Also, in this case the coefficients a_l may depend only on the b_l. Especially for an ideal gas, $b_1 = 1$ and $b_l = 0$ for $l \geq 2$, and correspondingly, $a_1 = 1$ and $a_l = 0$ for $l \geq 2$. We want to determine the coefficients a_l from the b_l. To this end, we multiply Equation (16.61) by λ^3/v and insert the series (16.58) on the right-hand side:

$$\frac{p\lambda^3}{kT} = \sum_{l=1}^{\infty} a_l \left[\sum_{n=1}^{\infty} n b_n z^n\right]^l = \sum_{l=1}^{\infty} b_l z^l \tag{16.62}$$

If one orders the first sum with respect to powers of z, a comparison of the coefficients directly yields the equations for the a_l:

$$\begin{aligned}
b_1 &= a_1 b_1 \\
b_2 &= a_1 2b_2 + a_2 b_1^2 \\
b_3 &= a_1 3b_3 + a_2 4b_1 b_2 + a_3 b_1^3 \\
b_4 &= a_1 4b_4 + a_2\left(4b_2^2 + 6b_1 b_3\right) + a_3 6b_1^2 b_2 + a_4 b_1^4 \\
&\vdots
\end{aligned} \tag{16.63}$$

These equations can be successively solved for the a_l:

$$
\begin{aligned}
a_1 &= b_1 = 1 \\
a_2 &= -b_2 = -\frac{2\pi}{\lambda^3}\int_0^\infty \left(\exp\left\{-\frac{U(r)}{kT}\right\} - 1\right) r^2\,dr \\
a_3 &= 4b_2^2 - 2b_3 \\
a_4 &= -20b_2^3 + 18b_2b_3 - 3b_4 \\
&\vdots
\end{aligned}
\tag{16.64}
$$

For sake of completeness, we want to denote a general expression for the a_l without derivation:

$$
a_l = -\frac{l-1}{l}\sum_{\{m_i\}}{}'(-1)^{\sum_i m_i - 1}\frac{\left(l - 2 + \sum_i m_i\right)!}{(l-1)!}\prod_i \frac{(ib_i)^{m_i}}{m_i!} \tag{16.65}
$$

The summation in Equation (16.65) runs over all sets $\{m_i\}$ which fulfill

$$
\sum_{i=2}^{l}(i-1)m_i = l - 1 \qquad m_i = 0, 1, 2, \ldots \tag{16.66}
$$

Equation (16.65) holds for $l \geq 2$, since trivially $a_1 = b_1 = 1$. If one restricts oneself to the first two terms, the virial expansion reads

$$
\frac{pV}{NkT} = 1 - b_2(T)\left(\frac{\lambda^3}{v}\right) \tag{16.67}
$$

This corresponds exactly to Equation (16.12), which we formerly obtained by much simpler reasoning ($a = 2b_2\lambda^3$). If one calculates the second virial coefficient $b_2(T)$ with the realistic Lennard–Jones potential, Example 16.1, one obtains

$$
b_2(T) = \frac{2\pi}{\lambda^3}\int_0^\infty \left[\exp\left\{-\frac{U_0}{kT}\left(\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^6\right)\right\} - 1\right] r^2\,dr \tag{16.68}
$$

Substituting $r' = r_0/r$, one has

$$
b_2(T)\lambda^3 = 2\pi r_0^3\int_0^\infty \left[\exp\left\{-\frac{U_0}{kT}\left(\left(\frac{1}{r'}\right)^{12} - 2\left(\frac{1}{r'}\right)^6\right)\right\} - 1\right] r'^2\,dr' \tag{16.69}
$$

Thus the quantity $B_2(T) = -b_2(T)\lambda^3/r_0^3$ is a dimensionless number which depends only on the parameter kT/U_0. If one now determines with the equation of state (16.67), the optimal parameters U_0 and r_0 for various gases, and plots $B_2(T)$ versus kT/U_0, one should obtain for all gases approximately the same curve, which also can be derived theoretically by a numerical evaluation of Equation (16.69). This curve was already presented in the thermodynamics part of this book: if one compares the experimentally found values for $B_2(T)$ with the theoretical result, one observes an astonishing agreement. For instance, for argon one obtains the values $r_0 = 3.82 \cdot 10^{-10}$ m and $U_0/k = 120$ K (Figure 1.8).

17 Classification of Phase Transitions

In this Chapter, we want to give an overview of a very young research field of statistical physics: the physics of phase transitions. In the first part of this book we have already mentioned phase transitions between solid, liquid, and gaseous aggregation states. In the following we also want to present other phase transitions, and to discuss advanced methods for their theoretical description. This should give the reader the ability to understand the original literature in quite different branches of this research area.

First we summarize the knowledge with respect to phase transitions that we have gained in the thermodynamics part of this book. According to Gibbs' phase rule (3.4) a homogeneous phase possesses two intensive degrees of freedom (as long as no additional degrees of freedom, like electric or magnetic dipole moments, play a role). Most often, one chooses pressure and temperature (but sometimes also T and μ). The third intensive variable is given by the Gibbs–Duhem relation (2.74).

Due to the postulate of coexistence of two phases (solid–liquid, solid–gaseous or liquid–gaseous) 3 of the initial 6 intensive variables can be eliminated via Gibbs' relations of phase equilibrium. Due to the Gibbs-Duhem relations (one for each phase), 1 intensive variable remains, which can be independently fixed (e.g., T). Then one calculates, for instance, the pressure p as a function of T, which leads to the melting, sublimation and vapor pressure curves in the pT diagram. All three phases coexist simultaneously at the crossing of the three curves, the triple point. Here all intensive variables of the system (T, p, μ) are fixed. There are 9 intensive variables, but also 6 Gibbs phase coexistence relations, and additionally 3 Gibbs-Duhem relations, so that the system of equations in the variables μ_i, T_i, and p_i, $i = 1, 2, 3$ has a unique solution (which corresponds to the triple point).

It is immediately clear that rearrangements of the structure are connected with the particular phase transitions, e.g., in water. For instance, in ice crystals there is an ordering of the water molecules over macroscopic distances, while in the liquid phase this order is lost. However, there is also a certain order in the liquid, since the water molecules (which are electric dipoles) mutually interact. Only in the gaseous phase is the mean distance between the molecules so large that this interaction plays no important role, and the particle motion is nearly free.

It can be shown that most rearangements of the structure in phase transitions can be described by a so-called *order parameter* (Landau, 1937). This order parameter, which we will generally denote by Ψ in the following, should represent the main qualitative difference between the various phases. This means in particular that it should vanish for the liquid–gas phase transition at the critical point, since then a distinction between both phases is no longer possible. In this case, e.g., the density difference $\Psi = \Delta\rho = \rho_l - \rho_g$ would be a suitable order parameter, as well as (for fixed particle number) the volume difference $V_g - V_l$ or the entropy difference.

It is often difficult to find a suitable order parameter for a certain phase transition. As we will soon see, for a qualitative understanding of many phase transitions it is already sufficient to know whether such a Ψ exists at all. In particular, the order parameter is small in the vicinity of the critical point and can thus serve as expansion parameter in the description of critical phenomena.

For a given temperature, phase transitions occur via changes of external parameters such as the volume, magnetic field, etc. Therefore one often describes phase transitions with the help of diagrams, where the respective external field is plotted against the order parameter.

The experimental investigation of, e.g., liquid–gas phase transitions is not without problems: at the critical point (or in the coexistence region) the compressibility as well as the specific heat and the volume expansion coefficient diverge; furthermore, the density difference between the gaseous and liquid phase vanishes. Due to the divergence of the heat capacity it is difficult to reach thermodynamic equilibrium in the vicinity of the critical point. Minor fluctuations in temperature lead to large changes of state. One has to control the temperature exactly at least up to $\Delta T/T \approx 10^{-2}$ to 10^{-3} to have an acceptable measurement error.

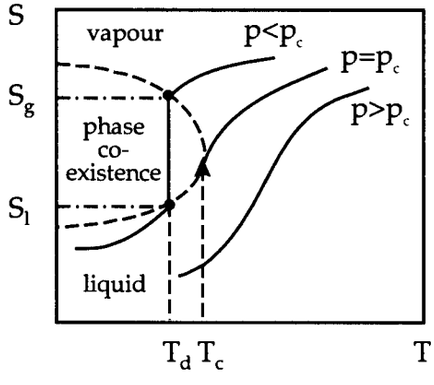


Figure 17.1. ST diagram.

Temperature deviations yield large changes of the volume, i.e., strong density fluctuations, due to the diverging expansion coefficient. Microscopically small drops are continuously formed which immediately evaporate again. Since the size of these droplets is of the order of the wavelength of visible light, there is a strong diffraction of light at the critical point (critical opalescence).

Phase transitions exhibit themselves dramatically in many thermodynamic state quantities in the form of discontinuities. For instance, the entropies of the liquid and the gaseous phase are very different (different degrees of order) in evaporation at constant pressure and at constant temperature (e.g., water: $p = 1.01325 \cdot 10^5$ Pa, $T_d = 100°\text{C}$), which in turn leads to a discontinuity of the entropy at the evaporation temperature $T_d(p)$ (cf. Figure 17.1).

The entropy difference $S_g - S_l$ corresponds, according to

$$\Delta Q = T_d(S_g - S_l) \tag{17.1}$$

to an amount of heat ΔQ, which has to be brought into the system at the evaporation temperature $T_d(p)$ to achieve the evaporation. ΔQ is the so-called *evaporation heat* or *latent heat*. If one heats water, for instance, water at atmospheric pressure, at first the

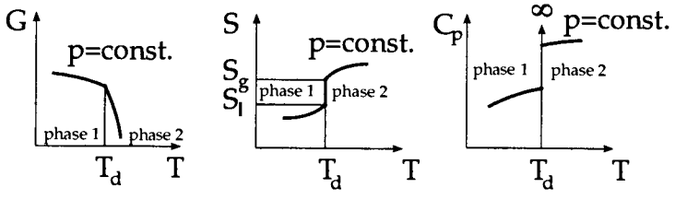


Figure 17.2. Free enthalpy, entropy, and specific heat as a function of temperature for a first-order phase transition.

temperature rises according to $\Delta Q = C_p^l \Delta T$, until the evaporation temperature $T_d(p)$ is reached (e.g., $T_d = 100°C$). Further heating, however, effects no further temperature increase, as long as not all of the liquid has evaporated. The additional energy serves to break up the remaining bonds between the water molecules and to increase the entropy from S_l to S_g. When all the liquid has evaporated, further heating effects again a temperature rise. This corresponds to an infinite heat capacity $C_p = T\partial S/\partial T|_p$ at the evaporation temperature.

Phase transitions which are connected with an entropy discontinuity are called *discontinuous* or *phase transitions of first order*. On the other hand, phase transitions where the entropy is continuous are called *continuous* or of *second* or *higher order*.

To achieve a more general and unique classification of phase transitions, one starts from the Gibbs' free enthalpy G (in the literature often one also uses the grand canonical potential Φ). It is convenient to consider the free enthalpy as a function of the natural variables, e.g., $G(N, T, p, \vec{H}, \vec{E}, \ldots)$. Apart from the particle number and the temperature, further intensive field variables appear like pressure, magnetic field, electric field, etc., which represent the state variables which can be externally controlled. Then the conjugated extensive quantities like entropy, volume, and magnetic and electric dipole moments assume values according to

$$\Psi = \pm \left.\frac{\partial G}{\partial h}\right|_{N,\ldots} \tag{17.2}$$

where we use the letter h for the relevant field variable and Ψ for the conjugated state quantity. This is, in general, related to the respective order parameter in a simple way, for which reason we use the same notation (e.g., pressure → volume, temperature → entropy, magnetic field → magnetic dipole moment, etc.).

For a first-order phase transition, one of the first derivatives of the free enthalpy with respect to the external fields is discontinuous:

$$S = -\left.\frac{\partial G}{\partial T}\right|_{N,p,\ldots} \qquad V = \left.\frac{\partial G}{\partial p}\right|_{N,T,\ldots} \qquad d_z = -\left.\frac{\partial G}{\partial H}\right|_{N,T,\ldots} \tag{17.3}$$

This discontinuity produces a divergence in the higher derivatives like the specific heat C_p, the compressibility κ, the expansion coefficient α, or the susceptibility χ (see Figure 17.2):

$$C_p = T \left.\frac{\partial S}{\partial T}\right|_p = -T \left.\frac{\partial^2 G}{\partial T^2}\right|_p$$

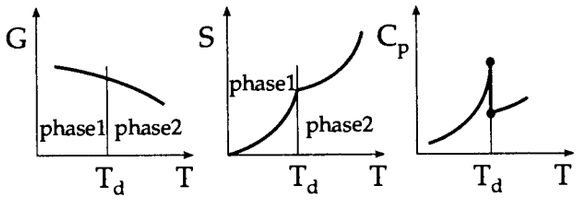


Figure 17.3. Free enthalpy, entropy, and specific heat as a function of temperature for a second-order phase transition.

$$\kappa = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_T = -\frac{1}{V}\left.\frac{\partial^2 G}{\partial p^2}\right|_T$$

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p = \frac{1}{V}\frac{\partial^2 G}{\partial p \partial T} \tag{17.4}$$

$$\chi = \left.\frac{\partial D_z}{\partial H}\right|_T = -\left.\frac{\partial^2 G}{\partial H^2}\right|_T$$

For instance, in the liquid–gas phase transition, C_p (as well as κ and α) diverges. One immediately anticipates this without calculation if one considers that in the coexistence of liquid and vapor the (vapor) pressure is a function of temperature, and for $T = \text{const.}$ it has to hold that $dp = 0$, or for $p = \text{const.}$, $dT = 0$.

Like evaporation, melting and sublimation are also phase transitions of first order, since they involve a latent heat. Note, however, that some processes which are called melting are not phase transitions in our sense. For instance, glass becomes viscous as it is heated up, and then becomes liquid. This corresponds to a continuous change of viscosity, in which no discontinuities appear. Furthermore, glass is not crystalline in the solid state, but shows an amorphous structure which does not change suddenly under heating. Thus, even at room temperature glass has actually to be considered to be a liquid (however, a liquid with an extremely large viscosity). The degree of order of glass does not change, in contrast to the solid–liquid phase transition of water (by the way, similar arguments apply also to many kinds of fats and other organic materials).

For a phase transition of second or nth order, the first derivatives of the free enthalpy are continuous; however, second derivatives like the specific heat or the susceptibility, or nth-order derivatives are discontinuous or divergent. In Figure 17.3 the discontinuity of the specific heat at T_d is due to a kink in the entropy.

The transition to superconductivity without an external magnetic field is an example of phase transitions of this kind. Essentially, most kinds of second-order phase transitions are not due to kinks in the entropy, but are due to a vertical tangent at $T = T_d$.

Because of the characteristic shape of the specific heat, such phase transitions are called *λ-transitions* (see Figure 17.4). An extraordinarily interesting example is the transition to superfluidity in ^4He (see Example 13.1). Further examples are rearrangements in alloys (order-disorder phase transitions), the transition to ferroelectricity in certain materials, and rearrangements of the orientation in crystal lattices.

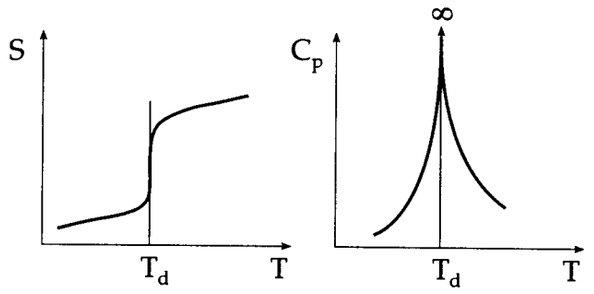


Figure 17.4. Entropy and specific heat as a function of temperature for a λ-transition.

A comparison of the figures shows a characteristic difference between the first-order phase transitions and the λ-transitions. For the latter, the onset of the phase transition can be anticipated even before the transition temperature is reached due to a strong increase of the specific heat C_p, while for first-order phase transitions C_p diverges only when both phases coexist. Note, however, that phase transitions of first order may become phase transitions of second order if the critical temperature is approached. For example, for $T < T_c$ the entropy is discontinuous in the liquid–vapor phase transition, but the discontinuity becomes smaller if one approaches T_c. Finally, for $T = T_c$ or $p = p_c$ the entropy discontinuity vanishes, and one obtains instead a vertical tangent, which corresponds to a λ-transition.

Thus, the order of a phase transition may depend on the specific conditions under which it is investigated. In any case, a phase transition is related to a nonanalytical behavior of the free enthalpy. Therefore, one can classify phase transitions, if one finds the points where the free enthalpy or the grand canonical potential become nonanalytical. However, this can be calculated from

$$\phi = -pV = -kT \ln \mathcal{Z} \qquad \text{with} \qquad \mathcal{Z}(z, V, T) = \sum_{N=0}^{\infty} z^N Z(N, V, T) \tag{17.5}$$

Unfortunately, in this framework one is able to treat only a few model systems with interactions explicitly.

However, with a method developed by Yang and Lee (1952) we can get an overview of how such nonanalyticities occur. To this end, we especially consider the liquid–vapor phase transition. The interaction potential between the particles is essentially of the shape of the Lennard–Jones potential or the Sutherland potential (see Example 16.1). For large densities, it follows that the canonical partition function

$$Z(T, V, N) = \frac{\lambda^{3N}}{N!} \int d^3 r_1 \cdots d^3 r_N \exp\left\{-\beta \sum_{i<k} U_{ik}\right\} \tag{17.6}$$

(for a given volume and very large particle numbers) must always vanish. Namely, for growing particle number the mean distance between particles becomes ever smaller, and in $\sum_{i<k} U_{ik}$ there are always more terms where the distance between the particles is small. That is, the corresponding U_{ik} are large, and the exponential factor in the integral becomes vanishingly small. Thus, the partition functions (17.6) contribute to (17.5) only as long as $N \leq N_{\max}(V) \approx V r_0^{-3}$, if r_0 denotes the range of the hard core of the potential. In this

case, the grand canonical partition function can be considered to be a polynomial of order $N_{\max}$ in the variable z. As one knows, such a polynomial can be decomposed into a product according to

$$\mathcal{Z}(z, V, T) = \sum_{N=0}^{N_{\max}} Z(N, V, T) z^N = \prod_{k=1}^{N_{max}} \left(1 - \frac{z}{z_k}\right) \tag{17.7}$$

if the z_k are the complex roots (Figure 17.5) of

$$\sum_{N=0}^{N_{\max}} Z(N, V, T) z^N = 0 \tag{17.8}$$

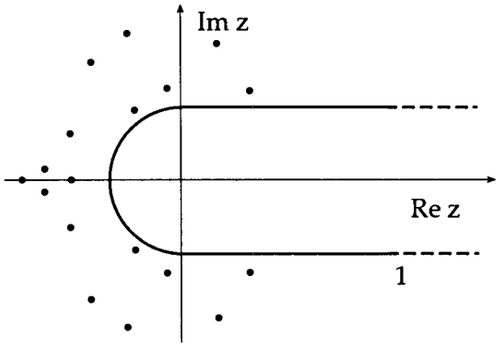


Figure 17.5. Distribution of the z_k in the complex z-plane.

Of course, these have to be pairwise complex conjugated, since the coefficients $Z(N, V, T)$ are real. The roots $z_k(V, T)$ are functions of V and T, and their number $N_{\max}(V)$ increases proportionally to the volume. Furthermore, the solutions of Equation (17.8) cannot be situated on the positive part of the real z-axis, since all $Z(N, V, T)$ are positive. From this fact one realizes that for finite volume or finite $N_{\max}(V)$, respectively, the grand canonical potential (17.5) or the pressure must show analytical behavior on the real axis. The function

$$-\frac{\phi}{V} = p = \frac{kT}{V} \ln \mathcal{Z} = \frac{kT}{V} \sum_{k=1}^{N_{\max}} \ln \left(1 - \frac{z}{z_k}\right) \tag{17.9}$$

is holomorphic for all $z_k \neq z$, hence especially on the real z-axis. However, in the thermodynamic limit, $V \to \infty$, $N \to \infty$, $\frac{N}{V} =$ const. ($N_{\max} \to \infty$), the number of z_k becomes infinite, so that these can come arbitrarily near the real axis. (See Figure 17.6.) Then the grand canonical potential is only piecewise analytical on the real z-axis (a function is called analytical in the point z if it can be expanded in a power series around z), and phase transitions can occur at certain places.

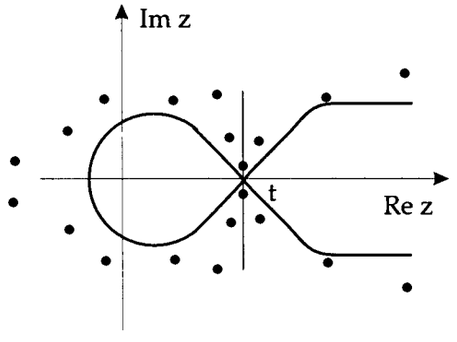


Figure 17.6. Distribution of the z_k in the thermodynamic limit for a phase transition.

Note that according to this consideration real (mathematical) nonanalyticities are possible only in the thermodynamic limit.

This means in particular that there are in a *strict* sense no phase transitions in small systems (a few particles), but for very small systems a statistical treatment is nevertheless a crude approximation.

However, even for finite particle numbers, the change in thermodynamic quantities can be so sudden that they cannot be distinguished at all from real nonanalyticities by

experimental means. According to Yang and Lee the limiting function

$$F(z, T) = \lim_{V \to \infty} \left(\frac{1}{V} \ln \mathcal{Z} \right) = \frac{p(z, T)}{kT} \tag{17.10}$$

has the following important properties:

1. It is well defined for all positive real z.
2. It is a continuous, monotonously increasing function of z.
3. It does not depend on the shape of the volume, as long as this is not formed in such a "pathological" manner that the surface grows faster than $V^{2/3}$.
4. The quantity $(1/V) \ln \mathcal{Z}$ converges uniformly for $V \to \infty$ toward the limiting function $F(z)$ in any region of analyticity.
5. The derivatives $\partial/\partial(\ln z)F(z)(\equiv 1/v$, which the reader may confirm as an exercise) are also analytical in the regions of analyticity of $F(z)$.

In the regions of analyticity of $F(z)$, the system behaves as a single homogeneous phase. The "equations of state" $p = kTF(z, T)$ (cf. Equation (17.10)) and $1/v = \frac{\partial}{\partial \ln z} F(z)$ are analytical and without discontinuities, as just discussed. If we enter regions where the roots z_k approach the real axis, the equations of state become unstable, which announces the transition to another phase. Phase coexistence is possible just at the boundary of the region of analyticity. In particular, the region around $z = 0$ is to be identified with the gaseous phase (for a classical ideal gas, $z = N\lambda^3/V \ll 1$).

By the way, from this one can derive an interesting relationship between the roots z_k and the cluster integrals $b_l(V, T)$ of Mayer's cluster expansion (see Chapter 16): If one expands the logarithm in Equation (17.9) around $z = 0$ in the region $|z/z_k| < 1$ for all k,

$$\frac{p}{kT} = \frac{1}{V} \sum_{k=1}^{N_{\max}} \left(-\sum_{l=1}^{\infty} \frac{1}{l} \left(\frac{z}{z_k} \right)^l \right) = \sum_{l=1}^{\infty} \left(-\frac{1}{Vl} \sum_{k=1}^{N_{\max}} \left(\frac{1}{z_k} \right)^l \right) z^l \tag{17.11}$$

one obtains by comparison with Equation (16.62),

$$b_l(V, T) = -\frac{\lambda^3}{Vl} \sum_{k=1}^{N_{\max}} \left(\frac{1}{z_k} \right)^l \tag{17.12}$$

It becomes obvious that the cluster expansion will correctly describe the gaseous phase in a certain range around $z = 0$; however, near a phase transition it must fail, since a power series expansion in z (like in Equation (17.12)) is no longer possible.

Theorem of corresponding states

In the section concerning the Maxwell construction we already have seen that the liquid–vapor phase transition can be described with the help of the van der Waals equation. If

one writes this equation of state in terms of the so-called reduced variables (cf. Equations (3.25–27)):

$$\overline{p} = \frac{p}{p_c} \qquad \overline{v} = \frac{v}{v_c}, \qquad \overline{T} = \frac{T}{T_c} \tag{17.13}$$

one obtains the following dimensionless equation:

$$\left(\overline{p} + \frac{3}{\overline{v}}\right)(3\overline{v} - 1) = 8\overline{T} \tag{17.14}$$

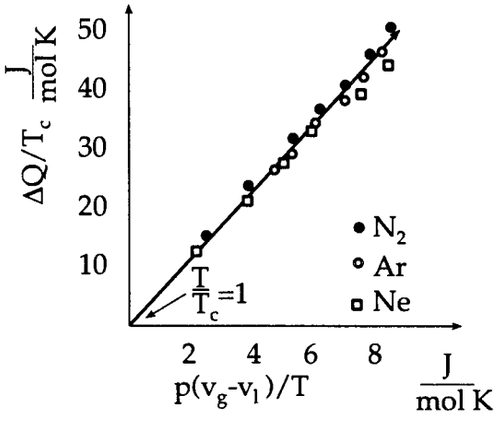


Figure 17.7. Reduced evaporation heat.

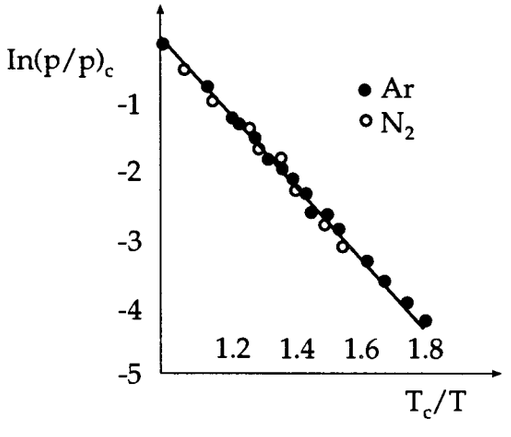


Figure 17.8. Evaporation pressure of simple liquids.

As one observes, no parameters occur which depend on the material. Therefore all "simple" real gases, which are described with sufficient accuracy by the van der Waals equation, obey the same equation of state (17.14) in reduced variables. Simple gases are, for instance, noble gases, N_2, O_2, H_2, CO, CH_4, etc.; i.e., gases which do not possess an electric dipole moment and whose atoms or molecules are not strongly correlated even in the liquid phase. This assertion which was first found by van der Waals is called the *theorem of corresponding states*.

Interestingly, analogous assertions hold also for many other properties of these gases. For instance, if one plots the reduced evaporation heat $\Delta Q/T_c$ versus $p(v_g - v_l)/T$, one finds experimentally a curve which is common to all simple gases and which is to good approximation a straight line with a slope of 5.4 (Figure 17.7):

$$\frac{\frac{\Delta Q}{T_c}}{\frac{p(v_g - v_l)}{T}} = 5.4 \tag{17.15}$$

for $0.5 < \frac{T}{T_c} < 1$

With this result the Clausius–Clapeyron equation for the temperature dependence of the vapor pressure can be written in the form

$$\frac{dp}{dT} = \frac{s_g - s_l}{v_g - v_l} = \frac{\Delta Q/T}{v_g - v_l} \tag{17.16}$$

$$\frac{\frac{dp}{p}}{\frac{dT}{T^2}} = \frac{\Delta Q}{\frac{p(v_g - v_l)}{T}} = \frac{\frac{\Delta Q}{T_c}T_c}{\frac{p(v_g - v_l)}{T}} = 5.4T_c \tag{17.17}$$

If one integrates this from T to T_c or from p to p_c, one obtains

$$\ln \frac{p}{p_c} = 5.4\left(1 - \frac{T_c}{T}\right) \qquad \text{for} \qquad 0.5 < \frac{T}{T_c} < 1 \tag{17.18}$$

Thus, the vapor pressure also has the same form in reduced variables for simple gases or liquids, which is excellently confirmed by the experiment (see Figure 17.8). By comparison with Example 3.2, one obtains, with respect to 1 mol,

$$\frac{\Delta Q}{RT_c} = 5.4 \tag{17.19}$$

However, this approximate relation between the evaporation heat and the critical temperature is valid only at a sufficiently large distance from the critical point ($0.5 < T/T_c < 0.7$), since we have assumed $v_g \gg v_l$ in Example 3.2.

Critical indices

A fundamental problem of the theory of phase transitions is the behavior of a system in the vicinity of the critical point. As we have already seen, several thermodynamic quantities begin to diverge at this point, and the order parameter vanishes. However, one can make this statement more precise, if one derives the behavior of the most important thermodynamic quantities in the vicinity of the critical point as a function of temperature. To this end one uses power laws, the exponents of which are called *critical indices*. For the liquid–vapor phase transition, one needs six critical indices, with the commonly used standard notations $\alpha, \alpha', \beta, \gamma, \gamma', \delta$. The order parameter $\rho_l - \rho_g$ vanishes for $T \to T_c$ like

$$\Psi = \rho_l - \rho_g \propto \left(1 - \frac{T}{T_c}\right)^{\beta} \tag{17.20}$$

The specific heat at the critical volume $C_{V=V_c}$ may diverge in different ways for $T \to T_c$, depending from which side one approaches the critical temperature:

$$C_{V=V_c} \propto \begin{cases} \left(\dfrac{T}{T_c} - 1\right)^{-\alpha} & \text{if } T|_{\rho \approx \rho_c} \geq T_c \\ \left(1 - \dfrac{T}{T_c}\right)^{-\alpha'} & \text{if } T|_{\rho \approx \rho_c} \leq T_c \end{cases} \tag{17.21}$$

A corresponding behavior is found for the compressibility,

$$\kappa \propto \begin{cases} \left(\dfrac{T}{T_c} - 1\right)^{-\gamma} & \text{if } T \geq T_c \\ \left(1 - \dfrac{T}{T_c}\right)^{-\gamma'} & \text{if } T \leq T_c \end{cases} \tag{17.22}$$

The last exponent describes the critical isotherm

$$p - p_c \propto |\rho - \rho_c|^{\delta} \qquad \text{for} \qquad T = T_c \tag{17.23}$$

The following table contains a few experimental values for the critical indices of simple gases.

Exponent	Ar	Xe	CO_2	^{3}He	^{4}He
α'	< 0.25	< 0.2	0.124	0.105	0.017
α	< 0.40	–	0.124	0.105	0.017
β	0.362	0.35	0.34	0.361	0.354
γ'	1.20	–	1.1	1.17	1.24
γ	1.20	1.3	1.35	1.17	1.24
δ	–	4.4	5.0	4.21	4.00

Also, in this case the simple gases show a very similar behavior, according to the theorem of corresponding states (only the indices α, α' of ^{4}He show strong deviations, which indicates that ^{4}He is by no means a simple fluid below the critical point $T_c \approx 5.2$ K). We have to note that the experimental determination of critical indices is very difficult, and may contain large errors.

Quite analogously, critical indices can be defined also for other phase transitions. It can be shown that many phase transitions of second order can be described by the same critical indices. In the following, we first want to give an overview of the wide field of phase transitions using various examples.

Examples for phase transitions

a. Magnetic phase transitions

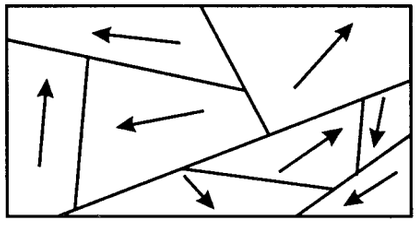


Figure 17.9. Weiss areas (schematically).

Certain materials like iron, cobalt, and nickel show ferromagnetic properties below a transition temperature T_c (Curie temperature). The same holds also for certain alloys from elements which are themselves not ferromagnetic (Cu_2MnAl, Cu_2MnSn). In comparison to paramagnetic behavior which is assumed above the Curie temperature, ferromagnetic materials are characterized by several peculiar properties. While field strengths of the order of 10^9 Am^{-1} are necessary to reach the saturation magnetization in a paramagnet, only a few 10^5 Am^{-1} are sufficient to achieve the same for a ferromagnet. The initial susceptibility of ferromagnetic materials is approximately nine orders of magnitude larger than that of paramagnets. After switching off the external field, a permanent dipole moment remains in ferromagnets which depends strongly on the prior mechanical and thermal treatment of the material. Ferromagnetism can be found only in solids with a well-defined crystalline structure.

According to P.A. Weiss (1907), the ferromagnetic pecularities are related to the fact that even in a nonmagnetized ferromagnet the atomic dipoles are not statistically distributed, but are aligned in larger areas of the order of tenths of millimeters (*Weiss areas*). (See Figure 17.9.)

These Weiss areas have therefore a spontaneous macroscopic dipole moment. However, in a nonmagnetized ferromagnet, the dipole moments of the single spontaneously magnetized Weiss areas are still statistically orientated, wherefore the material as a whole appears unmagnetized.

The spontaneous alignment of the atomic dipoles is due to the exchange interaction of the electrons, which mutually couples the magnetic moments. In the discussion of paramagnetism we were able to neglect this interaction.

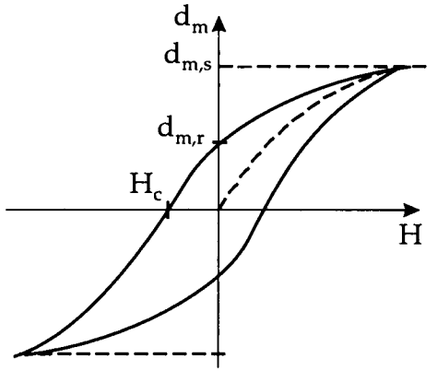


Figure 17.10. Hysteresis (the dashed curve represents the original curve of magnetization).

The spontaneous magnetization does not change abruptly between the single Weiss areas but continuously over a range of approximately 300 atoms (*Bloch walls*). If one puts an initially nonmagnetized ferromagnetic substance in an external magnetic field, the single dipoles are not aligned in a mutually independent manner against the temperature motion, but the aligned Weiss areas expand at the expense of the nonaligned areas via movements of the Bloch walls. In strong external fields, whole areas may spontaneously flip their total dipole moment. This explains the essentially larger susceptibility of ferromagnets and the small field strength necessary to achieve the saturation magnetization.

The movement of the Bloch walls may be considerably influenced by structural defects, impurities, crystal boundaries, etc. Thus the initial treatment of the material plays an important role.

After switching off the external magnetic field, a remanent magnetization $d_{m,r}$ of the material remains due to the coupling between the atomic dipoles. To remove this one has to apply a certain counter field H_c. The magnetization shows a strong hysteresis in dependence of the external field (see Figure 17.10).

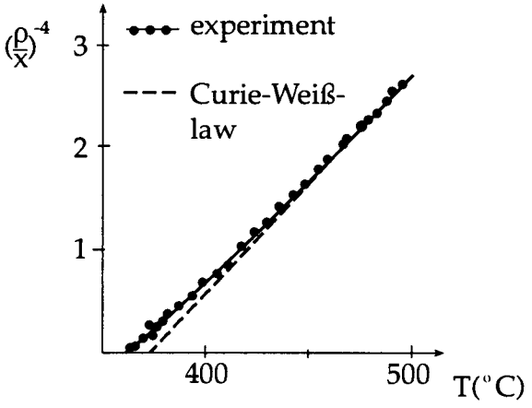


Figure 17.11. Reciprocal of the mass susceptibility of nickel in the vicinity of $T_c = 357°C$, $T_c' = 385°C$. ρ is the density.

The coupling energy of the atomic dipoles is on the order of 0.1 eV. If the temperature rises beyond a value corresponding to the thermal energy kT_c, the bonds are broken and the dipoles become statistically independent, which leads to paramagnetic behavior above T_c. Then, the Curie-Weiss law holds for the susceptibility,

$$\chi = \left.\frac{dd_m}{dH}\right|_T = \frac{C}{T - T_c'}, \qquad T \gg T_c \tag{17.24}$$

The temperature T_c' to be inserted in Equation (17.24) in most cases is considerably larger than the Curie temperature of the phase transition (e.g., nickel $T_c = 631K$, see Figure 17.11).

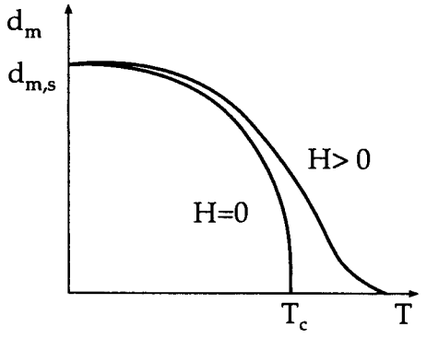


Figure 17.12. Spontaneous magnetization of the Weiss areas below the Curie temperature without ($H = 0$) and with a magnetic field ($H > 0$).

In the vicinity of the critical temperature T_c, the susceptibility can also be described in terms of critical indices,

$$\chi \propto \begin{cases} \left|1 - \dfrac{T}{T_c}\right|^{-\gamma} & \text{with } \gamma \approx 1.33 \quad \text{for} \quad T \geq T_c \\ \left(1 - \dfrac{T}{T_c}\right)^{-\gamma'} & \text{with } \gamma' \approx 1.33 \quad \text{for} \quad T \leq T_c \end{cases} \tag{17.25}$$

Below the Curie temperature T_c, a spontaneous magnetization of the Weiss areas is built up even without an external field (see Figure 17.12). In the case of small positive magnetic fields ($H \to 0^+$), the spontaneous magnetization is the order parameter of the phase transition. For $T \to T_c$ it vanishes like

$$d_m(T, H \to 0^+) \propto \left(1 - \frac{T}{T_c}\right)^{\beta} \quad \text{with } \beta \approx 0.33 \tag{17.26}$$

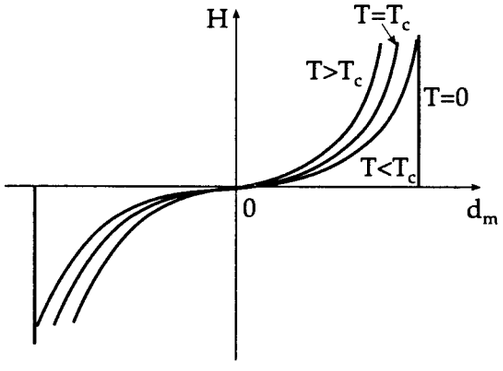


Figure 17.13. Isotherms of an ideal ferromagnet.

The critical index β of the order parameter has nearly the same value as for the liquid–vapor phase transition, and the values for γ and γ' are also on the order of the previously found values.

For $T = T_c$, the order parameter and the phase transition are continuous. For $T < T_c$, the magnetization jumps as a function of the external field, and the phase transition is of first order.

If one plots the magnetization d_m versus the magnetic field strength at constant temperature, one obtains schematically (without the hysteresis branches) Figure 17.13, which is quite analogous to the diagram for the liquid–vapor phase transition.

From the two last figures one can construct the schematic phase diagram of an ideal ferromagnet (Figure 17.14). The critical isotherm $T = T_c$ can be described by

$$H \propto |d_m|^{\delta} \quad \text{for} \quad T = T_c, \quad d_m \approx 0 \quad \text{with } \delta \approx 4.2 \tag{17.27}$$

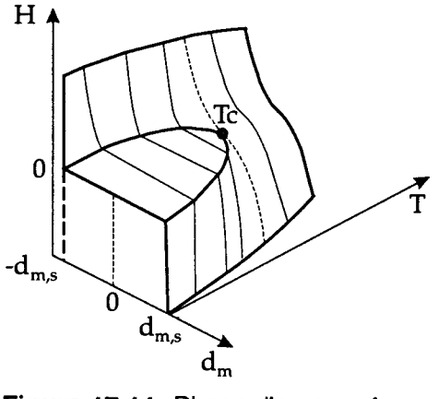


Figure 17.14. Phase diagram of an ideal ferromagnet.

in analogy to Equation (17.23). Also, this critical index agrees well with the corresponding index for the liquid–vapor phase transition. One finds that this (approximate) agreement of the critical indices happens for many phase transitions of second order (for $T = T_c$, the

liquid–vapor, as well as the paramagnetic– ferromagnetic phase transition, is of second order).

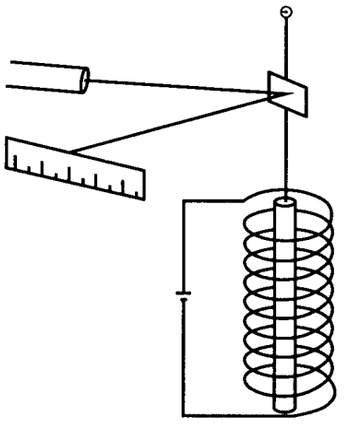


Figure 17.15. Experiment of Einstein and De Haas.

Hence, phase transitions of second order show an approximately universal behavior which does not depend on the details of the interaction, but only on a few global properties of the system, like dimension, number of components, and range of the interaction. Only after *renormalization group theory* was developed (K. Wilson, 1971), which also gained large importance in quantum field theory, was it possible to establish this universality hypothesis (Fisher 1966, Griffiths 1971) from the theoretical point of view.

In the following we want to study some important microscopic properties of magnetic phase transformations.

According to Equation (8.40), the atomic magnetic moment is proportional to the total angular momentum. If a magnetized piece of iron is remagnetized in a strong counter field, this causes a change of the angular momentum of the iron. If the iron rod is fixed so that it can freely rotate, the torque moment corresponding to the change of angular momentum rotates the rod.

This effect, which was first investigated by Einstein and De Haas (1915), allows for a determination of the gyromagnetic factor g (Figure 17.15). The experimentally found value $g \approx 2$ asserts, according to Equation (8.40), that the atomic moments contributing to the magnetization are solely due to the spin of the electrons ($j = s, l = 0$). Obviously, only between the spins of the electrons is there an interaction which is sufficiently strong to enforce a spontaneous alignment of the moments. This interaction, however, is not the classical magnetic dipole–dipole interaction, which would be far too weak, but rather is the quantum mechanical exchange interaction. The interaction energy of two electrons is quantum mechanically given by two parts due to the *antisymmetrization of the two-particle wavefunction*, the direct and the exchange interactions (see also Volume 1 of this series):

$$K_{ij} = \int \Psi_i^*(1)\Psi_j^*(2)U_{ij}\Psi_j(2)\Psi_i(1)d^3\vec{r}_1\, d^3\vec{r}_2 \quad \text{Direct}$$

$$I_{ij} = \int \Psi_j^*(1)\Psi_i^*(2)U_{ij}\Psi_j(2)\Psi_i(1)d^3\vec{r}_1\, d^3\vec{r}_2 \quad \text{Exchange} \qquad \textbf{(17.28)}$$

The interaction energy is $K_{ij} \pm I_{ij}$, where the $+$ holds for antiparallel spins and the $-$ for parallel spins. The energy difference between the configuration with parallel spins and that with antiparallel spins is

$$\epsilon_{\uparrow\uparrow} - \epsilon_{\uparrow\downarrow} = -2I_{ij} \qquad \textbf{(17.29)}$$

If $I_{ij} > 0$, a parallel alignment of the spins is preferred; and for $I_{ij} < 0$, an antiparallel alignment (Figure 17.16). It now becomes obvious that ferromagnetism can occur only in materials which have sufficiently many electrons with unpaired spins, whose contributions do not cancel. Furthermore, the overlap of the wavefunctions has to be large enough that I_{ij} assumes sufficiently large values. The exchange interaction

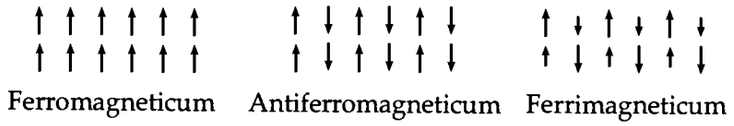


Figure 17.16. Schematic representation of various magnetic systems.

decreases rapidly with increasing distance between the electrons; thus in practice only the nearest neighbour atoms of a certain atom in the crystal lattice contribute to the interaction.

In iron, nickel, and cobalt the unpaired $3d$ electrons are responsible for the ferromagnetic behavior. Manganese even possesses 5 unpaired $3d$ electrons; however, it is not ferromagnetic; nevertheless, many manganese alloys like MnAs, MnBi, and MnSb are ferromagnetic.

From the measurement of the saturation magnetization of iron, with four unpaired $3d$ electrons, one obtains a mean magnetic moment of 2.2 μ_B per atom. Hence, on the average, 2.2 electrons per atom contribute to the magnetization.

The domain structure of the ferromagnet can be understood if one considers that the system wants to minimize the free energy for a given temperature; i.e., it wants to minimize the energy and maximize the entropy. However, not only the exchange energy contributes to the free energy, but also the magnetic field energy. If the whole material were uniformly magnetized, the latter would be very large, and could cancel the energy minimization due to the parallel alignment of the spins. On the other hand, if the material is separated into many spontaneously magnetized regions, not only is the magnetic energy reduced, but also the entropy is increased.

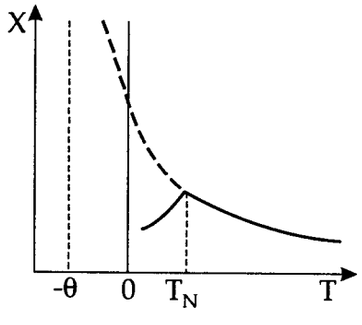


Figure 17.17. Susceptibility of an antiferromagnet.

Just as a strongly positive exchange integral I_{ij} enforces a parallel alignment of the spins, a strongly negative I_{ij} leads to an antiparallel alignment. Materials with a spontaneous antiparallel alignment of the magnetic moments are called *antiferromagnetic materials*. Antiferromagnetism is observed only up to a temperature analogous to the Curie temperature, the so-called *Néel temperature*.

At the Néel temperature a phase transition to paramagnetic behavior sets in. Of course, antiferromagnetic materials do not show a spontaneous magnetization; however, the phase transition exhibits itself by a kink in the susceptibility (Figure 17.17). Above the Néel temperature a behavior similar to the Curie-Weiss law holds,

$$\chi = \frac{C}{T + \Theta} \qquad \text{for} \quad T \gg T_N \tag{17.30}$$

If the antiparallel dipole moments of neighboring atoms (e.g., different atoms in alloys) have different values, a spontaneous magnetization can occur. Such materials are called *ferrimagnets*. They have a much smaller saturation magnetization than ferromagnetic materials. Their hysteresis curves can be influenced in wide regions by implementation of other atoms. Furthermore, many ferrimagnetic materials are nearly insulators. Thus,

they are used in transformers and solenoids, since they do not cause losses due to turbulent currents.

b. Order–disorder phase transitions

For phase transitions of this kind, the low-temperature phase possesses a certain order of the atoms or molecules which vanishes above the transition temperature. Order refers here to the order of the atoms or molecules in a crystal lattice (position order), or to the relative mutual orientation of certain molecules (orientation order). In principle, the solid–liquid and solid–vapor transitions also belong to these phase transitions. However, it is conventional to consider only solid–solid phase transitions in this category (since otherwise nearly all phase transitions would belong to this class).

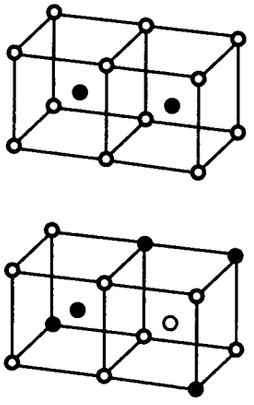


Figure 17.18. Structures of β–brass; above, ordered; below, statistically distributed.

Position order

Besides various rearrangements of the crystal structure, changes in the order of the atoms on the lattice sites also happen in some alloys, e.g., of type AB (CuZn) or A_3B (Cu_3Au). The phase transition in β-brass (CuZn) at $T = 465°C$ has been known for a long time. In the low-temperature phase brass possesses a CsCl structure, where copper and zinc are sited in a well-ordered manner in different sublattices (Figure 17.18).

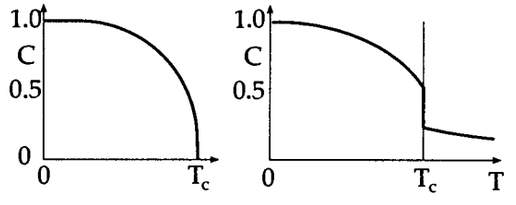


Figure 17.19. Temperature dependence of the order parameter, for a) β–brass b) alloys of type AB_3.

However, above the transition temperature, β-brass transforms to a cubic space-centered structure with statistically distributed Cu and Zn atoms. The characteristic form of the specific heat of β-brass near the transition points indicates a λ-transition (second order) (Figure 17.20). The order parameter is here the mean fraction of ordered layers (Figure 17.19). More precisely: let there be N A-atoms and N B-atoms in the alloy. The number of A-atoms in sublattice 1 is $\frac{1}{2}(1 + r)N$. Consequently, there have to be $\frac{1}{2}(1 - r)N$ A-atoms in sublattice 2.

The remaining free lattice sites of the two sublattices are then occupied by B-atoms, for instance, $\frac{1}{2}(1 - r)N$ B-atoms in sublattice 1 and $\frac{1}{2}(1 + r)N$ B-atoms in sublattice 2. The quantity r just vanishes, if A- and B-atoms are statistically distributed on both sublattices in a uniform way, and it holds that $r = \pm 1$, if sublattice 1 contains only A- or B-atoms, respectively.

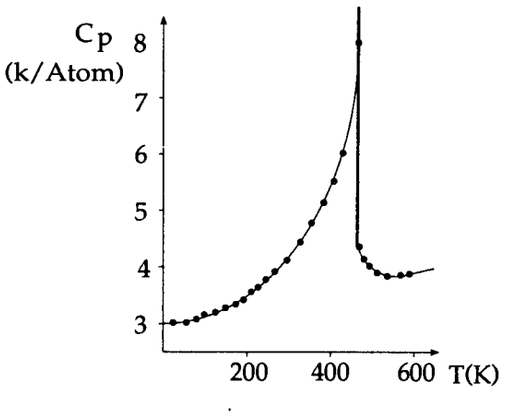


Figure 17.20. Specific heat of β-brass.

In contrast to alloys of type AB, the respective phase transitions in alloys of type AB_3 are of first order. The order parameter has a discontinuity T_c , and the phase transition is connected with a latent heat.

Orientation order

A typical example of orientation order can be found in $NaNO_2$. In the low-temperature phase ($T_c = 163°C$), the NO_2^- molecules are aligned with respect to the molecule plane.

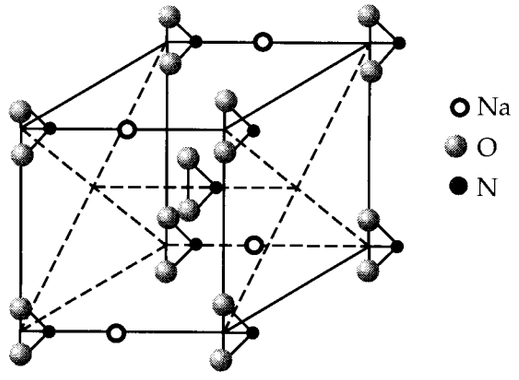


Figure 17.21. Orthorhombic unit cell of $NaNO_2$ in the ferroelectrical phase.

However, for $T > T_c$ they can rotate freely around the oxygen axis and are completely statistically oriented. Since the NO_2^- molecule has a strong electric dipole moment, a spontaneous (macroscopic) electric dipole moment arises in the low-temperature phase (Figure 17.21).

In analogy to the ferromagnetic media one calls materials with a spontaneous orientation of the permanent electrical dipole moments *ferroelectric materials*. The order parameter is the mean orientation of the NO_2^- molecules.

Other examples of orientation order are the ammoniumhalogenides NH_4Cl, NH_4Br, and NH_4J.

The NH_4^+ tetrahedra can assume two different orientations in the crystal lattice (see Figure 17.22). Above the critical temperature, both are statistically distributed; below $T_c = 256K$, all tetrahedra in NH_4Cl have the same orientation, while in NH_4Br below T_c the tetrahedra assume an alternating orientation.

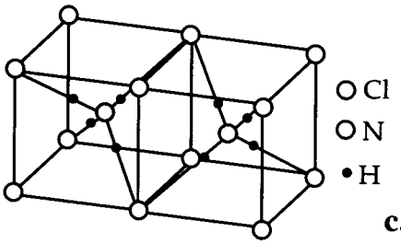


Figure 17.22. Possible orientations of the NH_4^+ tetrahedra in NH_4Cl.

c. Dislocation and ferroelectric phase transitions

This type of phase transition is a mutual displacement of atoms or molecules of a crystal lattice. These displacements happen in the direction of the eigenvector of a normal oscillation (the corresponding generalized coordinate is q), the potential of which changes with temperature (see Figure 17.23). One also speaks of a "softening" of a lattice oscillation or of *condensation of the corresponding phonons*. At T_c the second derivative of the potential energy vanishes at $q = 0$. For $T < T_c$, there are new stable equilibria for the respective particles. The corresponding elongation q_0 can be connected with an electric dipole moment (polar optical phonon).

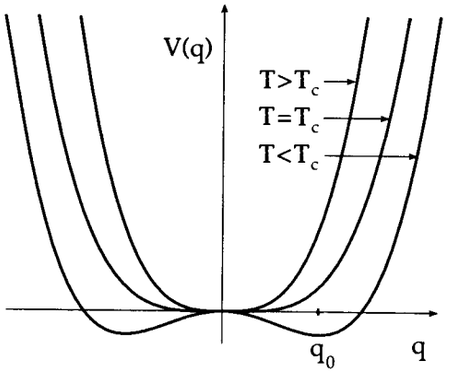


Figure 17.23. Anharmonic, temperature-dependent potential.

In this case, a spontaneous electric polarization occurs below the transition temperature, i.e., ferroelectric or antiferroelectric behavior, depending on whether the dipole moments are aligned parallel or antiparallel from one elementary cell to the next. For $T > T_c$, the dielectric constant drops with temperature, analogous to the paramagnetic susceptibility (paraelectric phase).

An example of a dislocation phase transition with ferroelectric properties is Bariumtitanate ($BaTiO_3$). The elongation of the ions for $T < T_c$ is illustrated in Figure 17.24. The dipole moment per elementary cell is of the order of $D_e \approx 1.04 \cdot 10^{-10} e$ m, which corresponds to a displacement of the Ba^{2+} and Ti^{4+} ions with respect to the O^{2-} ions of approximately $0.15 \cdot 10^{-10}$ m.

Examples of antiferroelectric materials are the perovskites $PbZrO_3$ and $PbHfO_3$. Purely dislocation or purely order–disorder phase transitions are limiting cases. One often finds mixed types of phase transitions, where several atoms

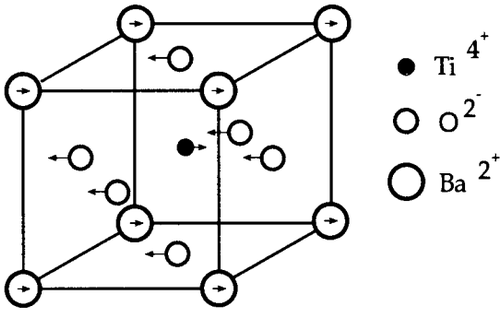


Figure 17.24. Displacement of ions in $BaTiO_3$.

are displaced and others assume an orientation or position order.

d. Rearrangements of the crystal structure

The solid phases of many materials may assume different crystal structures, depending on the pressure or the temperature (for alloys, also depending on the decomposition).

For instance, for ice at pressures up to $8 \cdot 10^8$ Pa six different modifications are known (ice I ... ice VI), where the usual ice at $p \approx 10^5$ Pa is only one of these structures.

Some nonmetals can even transform to a metallic phase at extremely high pressures. If there is no appropriate catalyst present, the solid–solid phase transitions may sometimes happen extremely slowly. For example, diamond is actually not stable at atmospheric pressure (see Figure 17.25). Tin transforms below 13.2 °C from a metallic phase with tetragonal symmetry (β-Sn) to a semiconducting phase with diamond structure (α-Sn), but this also happens extremely slowly (tin pestilence).

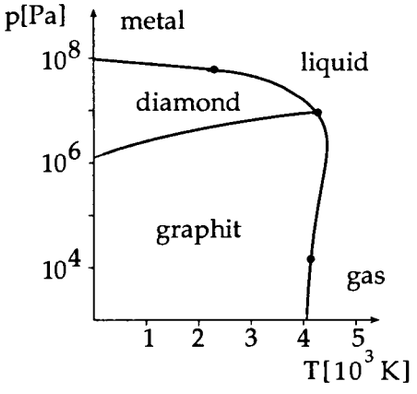


Figure 17.25. Phase diagram of ^{12}C.

e. Liquid crystals

In some organic materials with high molecular weight and a long, stretched form of the molecules, the long-distance order of the molecules is not lost in the melting process. Even in the liquid phase the molecules assume a certain order, which can be described by a position-dependent orientation vector $\vec{n}(x, y, z)$. In contrast to normal liquids, liquid crystals are therefore not isotropic. Depending on the kind of orientation, one distinguishes different forms (Figure 17.26). In the nematic phase the molecules assume a certain preferred direction, e.g., the z-direction, but there is no correlation in the x- or y-directions.

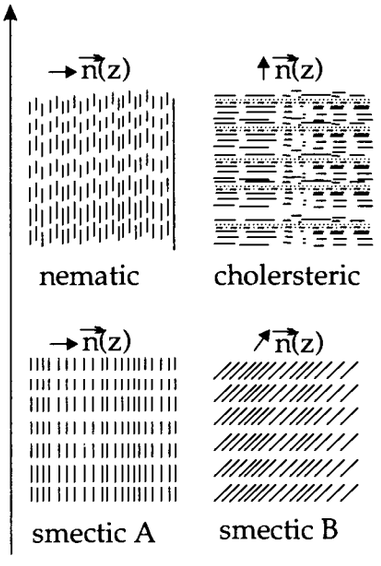


Figure 17.26. Structures of liquid crystals.

On the other hand, the smectic phases form layers with a preferred direction of the molecules, where a lot of further substructures occur. The layers may glide on each other. Inside a layer the molecules can be arbitrarily distributed without correlations in the xy-direction (smectic A), which leads to a two-dimensional liquid, or they may form rows with a certain correlation in the xy-direction (smectic B), which corresponds to two-dimensional crystals. In cholesteric liquid crystals the molecules are ordered screwlike. The coordinate dependence of the orientation vector $\vec{n}$ is of the form

$$n_x = \cos\left(\frac{2\pi}{L}z + \phi\right) \qquad n_y = \sin\left(\frac{2\pi}{L}z + \phi\right) \qquad n_z = 0 \tag{17.31}$$

The screw period L depends strongly on the temperature and on external electric or magnetic fields. At the critical temperature or at the critical field strength,

L becomes infinite. The Bragg reflections at the particular layers lead to impressively glittering color effects for cholesteric materials.

Some materials may assume several liquid crystal forms with increasing temperature. They have several transition temperatures.

In general, only complex organic materials form liquid crystals. Many of them have transition temperatures or melting points around 100 °C. At room temperature they have the consistency of viscous fats rather than of crystalline solids.

Only after researchers succeeded in producing materials with transition temperatures of the order of a few degrees Celsius, did liquid crystals become interesting from a technical point of view. The optical anisotropy of nematic liquid crystals leads to a strong reflection of light. At the phase transition to the isotropic liquid the reflection vanishes. In liquid crystals with a sufficiently large dipole moment, the permeability of light or the reflectivity can be simply and nearly powerlessly controlled by an electric field. These materials have gained large technical importance in liquid crystal displays (LCDs).

Macroscopic quantum effects: superconductivity and superfluidity

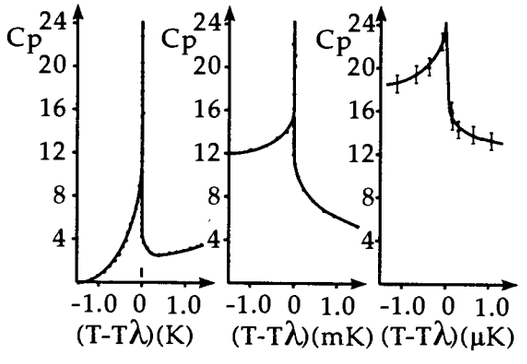


Figure 17.27. Specific heat of ^{4}He at the λ–point $T_\lambda = 2.171$K, according to Fairbank (1957).

Here we want to give an overview of the physics of superconductivity in certain metals below the critical temperature T_c, and of the transition to superfluidity in liquid ^{4}He at the λ-point. The latter is one of the most prominent examples for a λ-transition of second order. Note the characteristic form of the specific heat at the λ-point shown in Figure 17.27. The temperature resolution is successively increased by three orders of magnitude in the three pictures. In this case the order parameter is the thermodynamic average of the condensate wavefunction Ψ of the superfluid phase. The density of this phase is related to the order parameter via $\rho_s \propto |\Psi|^2$. When approaching the λ-point from small temperatures the order parameter should vanish like $(1 - T/T_\lambda)^\beta$, in analogy to Equation (17.20).

Experimentally, one finds $\beta \approx 0.33$, which again confirms the universality of phase transitions of second order. Especially, one can see that the wavefunction itself, and not the density, is the order parameter. For the latter, we would obtain $\beta = 0.66$.

From our considerations concerning the condensation of an ideal Bose gas, we can obtain an estimate for the parameter β. According to Equation (13.34), we have

$$\rho_s \propto 1 - (T/T_\lambda)^{3/2}$$

$$\propto 1 - (1 + (T - T_\lambda)/T_\lambda)^{3/2} \approx \frac{3}{2}(1 - T/T_\lambda) \qquad (17.32)$$

which implies $\beta \approx 0.5$ ($\Psi \propto \rho_s^{1/2}$).

Quite analogously, in the case of superconductivity the order parameter is given by the thermodynamic average of the wavefunction of the superconducting Cooper pairs. These are created by the (relatively weak) interaction of the metal electrons

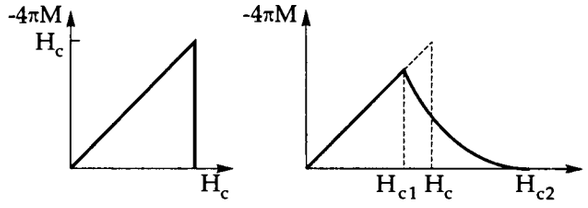


Figure 17.28. Magnetization curves for superconductors of the first and second kinds.

with the phonons of the lattice oscillations. In the normal conducting phase, scattering processes of the electrons with the phonons (or the oscillating ions, respectively) are responsible for the nonvanishing resistance of the metals. In these processes the ordered kinetic energy of the electron current transforms into a statistical excitation of lattice oscillations (heat). At low temperatures, the exchange of phonons between two electrons may, however, also lead to a bound state (*Cooper pair*). One electron deforms the ion lattice, and the other electron exploits the attraction of the (positive) ions which are shifted from their equilibrium position. It happens that this interaction is especially large for electrons with opposite momenta and antiparallel spins.

The bound states are separated from the free one-particle states by an energy *gap*. Even with a certain kinetic energy, a Cooper pair may be energetically favored in comparison with two free electrons without kinetic energy. In this case, the breakup of the Cooper pair via a scattering of an electron from a free phonon would lead to an energy increase, and thus does not happen. Only if a kinetic energy (critical current strength), which is equal to the energy gap, is surpassed, are one-particle scatterings possible, and the superconducting state breaks down.

For this reason, the materials which conduct especially poorly in the normal conducting state, like lead, show particularly high transition temperatures. In these materials the strong electron–phonon interaction leads to a large energy gap, so that the superconducting phase is still stable at larger temperatures.

This qualitative explanation of the superconducting state is quantum mechanically precisely founded in the theory of Bardeen, Cooper, and Schrieffer (BCS theory), and of Bogolyubov.

Superconductors are not only conductors with vanishing electrical resistance. Up to a limiting magnetic field strength H_c they also show the behavior of an ideal diamagnet: an external magnetic field is completely screened via induction of a counter magnetization inside the superconductor. This screening also happens if the magnetic field penetrates the material in the normal conducting state, and if the material is afterwards cooled below the transition temperature (*Meissner–Ochsenfeld effect*).

One distinguishes two categories of superconductors due to their behavior in external magnetic fields (see Figure 17.28). Superconductors of the first kind show the following magnetization curve: the superconducting state breaks down suddenly when the limiting field strength H_c is reached, and the order parameter has a discontinuity as a function of H for $T < T_c$.

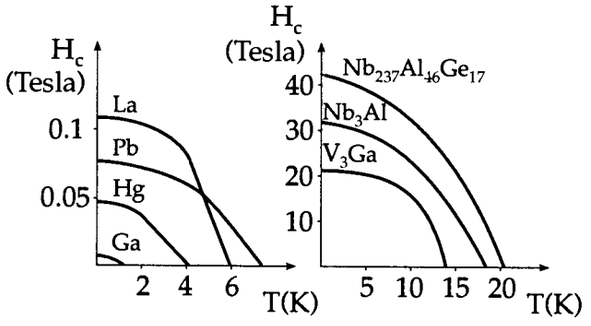


Figure 17.29. Temperature dependence of the limiting field strength for several superconductors of the first and second kinds.

For superconductors of the second kind (mostly alloys or transition metals with high resistance in the normal state), the magnetic field starts to penetrate the material at a critical field strength H_{c1}. However, all the Cooper pairs do not break up suddenly, but their number decreases with increasing field strength, until at a field strength H_{c2} the normal conducting state is reached.

If one has a superconductor of the first kind (e.g., lead) and alloys it with, e.g., indium, one obtains a superconductor of the second kind. The critical field strength H_{c1} drops with increasing indium content, and H_{c2} grows. However, the area below the magnetization curve is conserved. The dependence of the limiting field strengths H_{c1} and H_{c2}, respectively, for both types is shown in Figure 17.29.

The entropy of superconductors is smaller than that of the same materials in the normal conducting state, which can be reached below the transition temperature in the presence of a magnetic field $H > H_c(T)$. At $T = T_c$ the entropy shows a kink which corresponds to a discontinuity in the specific heat (Figure 17.30).

Thus, the transition to the superconducting state is an example of a phase transition of second order, which is, however, not a λ-transition.

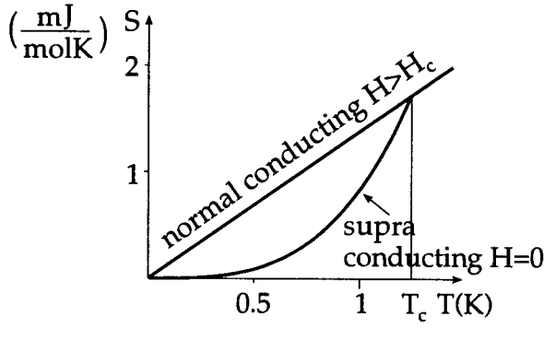


Figure 17.30. Entropy of superconductors.

18 The Models of Ising and Heisenberg

The theoretical description of phase transitions is very difficult. We have already explained some reasons for this in the preceding sections. Only a few models can be treated in the framework of statistical mechanics without large numerical efforts. One is due to Lenz (1920), and was later on worked out in detail by his pupil Ising (1925). Originally, it was invented for the phase transition of ferromagnets at the Curie temperature; however, in the course of time it was realized that with only slight changes the model can also be applied to other phase transitions, like order–disorder transitions in binary alloys. Furthermore, the model may be applied to several modern problems of many-particle physics, for instance for the description of so-called spin glasses. These are metals having amorphous instead of crystalline structures, which have the interesting property of nonvanishing entropy at $T = 0$. Recently, it has been realized that Ising's idea (in modified form) could also explain pattern recognition in schematic neural networks. Thus, this model gains more and more importance for the development of models for the human brain.

Ising's model mainly consists of a lattice of spins (magnetic moments), which can assume only two orientations, $\sigma = \pm 1$ with respect to the z-axis. According to Equation (17.29), there is an interaction between neighboring spins, in contrast to a paramagnetic system, and the interaction is such that parallel spins correspond to an energy $-I$ and antiparallel spins to an energy $+I$. Since the exchange interaction decreases rapidly with distance, we need to consider only nearest neighbors in the lattice. Since the parallel orientation of the spins is energetically favorable, this interaction leads to an enhanced parallel alignment of the spins. On the other hand, if the value of the exchange integral I is negative, antiparallel alignment is preferred.

The Hamiltonian thus reads, at first without an external magnetic field:

$$H(\sigma_1, \ldots, \sigma_N) = -I \sum_{n.n.} \sigma_i \sigma_k \qquad \sigma = \pm 1 \tag{18.1}$$

where one has to sum over all pairs of nearest neighbors. It is clear that the structure of the Hamiltonian depends on the coordination number q of the lattice (the number of nearest neighbors).

At $T = 0$, all spins will be aligned parallel, which leads to a magnetic dipole moment $D = N\mu$, if each spin carries the dipole moment μ. On the other hand, at large temperatures $kT \gg I$, the interaction plays no role, and due to the higher entropy a statistical orientation of the spins will be preferred. However, it is yet not obvious that this model system really exhibits a phase transition at a certain temperature T_c (which will depend on I), since the magnetization could also vanish continuously with increasing temperature.

To decide this question, one "simply" has to calculate the partition function belonging to Equation (18.1). However, one finds that this calculation is very difficult even for the most simple three-dimensional lattices. To date, there exists no analytical solution for the three-dimensional Ising lattice, but merely computer simulations as well as some very good approximative procedures based on the renormalization group theory developed by K. Wilson (1971). However, for the one-dimensional case the solution is relatively simple, and was calculated by Ising. Interestingly enough, the one-dimensional problem shows no phase transition to ferromagnetic behavior (i.e., $T_c = 0$), as we will see in the next Example. For this reason, Ising first considered his model as useless for describing ferromagnets. Heisenberg proposed an improved model (1928) which was based completely on the quantum mechanics developed up to this date. The Hamiltonian of the Heisenberg model is

$$\hat{H}(\vec{s}_1, \ldots, \vec{s}_N) = -2I \sum_{n.n.} \hat{\vec{s}}_i \cdot \hat{\vec{s}}_k \tag{18.2}$$

It contains, in contrast to Equation (18.1), the complete spin vectors of the interacting electrons of neighboring atoms. The additional factor 2 ensures that the meaning of I is the same in both models. In general, it holds that

$$\begin{aligned} 2\vec{s}_i \cdot \vec{s}_k &= \vec{S}^2 - \vec{s}_i^2 - \vec{s}_k^2 = S(S+1) - 2s(s+1) \\ &= S(S+1) - \frac{3}{2} \end{aligned} \tag{18.3}$$

if $s = \frac{1}{2}$ is the spin of the electrons which couple to a total spin $S = 0, 1$. For parallel spins ($S = 1$), one then obtains $H_{ik} = -\frac{1}{2}I$, and for antiparallel ($S = 0$), $H_{ik} = \frac{3}{2}I$. The energy difference $H_{\uparrow\uparrow} - H_{\uparrow\downarrow} = -2I$ is thus the same as in the Ising model.

If we neglect the x- and y-components of the spin vectors in Equation (18.2), whose expectation values vanish anyway, we obtain the Ising model, however, with the z-components of the spin operators as variables, which leads to an additional factor $\frac{1}{2}$ because $|s_z| = \frac{1}{2}$ and $|s_{iz}s_{kz}| = \frac{1}{4}$.

Once the Ising model was far better motivated, researchers tried more extensively to solve this model for lattices with a higher coordination number. In 1936 Peierls was able to show that the Ising model should exhibit ferromagnetic properties at low temperatures in higher dimensions, while these properties vanish in the one-dimensional case even for arbitrarily small temperatures. After Kramers and Wannier worked out an elegant way to solve the Ising model (1941), which also enabled them to achieve initial results for the two-dimensional case, Onsager succeeded in calculating the exact expression for the partition function of the two-dimensional Ising model without an external magnetic field (1944).

This solution is of great importance, since it represents one of the few cases where an exact solution is possible and which shows a phase transition.

In the meantime, a lot of approximations were investigated which also admit simple solutions in the three-dimensional case. Pierre Weiss postulated the existence of a molecular field in his investigations concerning ferromagnetism (1907), which should be responsible for the alignment of the magnetic moments, but the origin of which was completely unknown. This was the foundation of the molecular-field approximation (or mean-field approximation). One replaces the influence of all neighboring spins on a certain spin by a mean field which follows from the average orientation of the neighboring spins.

By the way, this approximation is well known from many other fields of physics. It corresponds, e.g., to the Hartree–Fock approximation in many-body problems, and to the replacement of field operators by their expectation values in quantum field theories. An approximation equivalent to the mean-field approximation is due to Bragg and Williams (1934, 1935). They studied order–disorder transitions in binary alloys. They realized that the energy of a certain atom does not depend so much on the details of its actual vicinity in the crystal lattice as on the average degree of order of the crystal. The average degree of order plays here the same role as the mean field of Weiss.

Based on these ideas, Bethe (1935) and Rushbrooks (1938) were able to find an improved approximation to the solution of the Ising model. The interaction of a central spin with its nearest neighbors is treated exactly, and only the interaction of these neighboring spins with the spins further away is replaced by the mean-field approximation.

From today's point of view, the Ising model is only a very schematic and crude approximation for the complicated spin wave interactions, which are the fundament of modern theories of ferromagnetism. However, it is of great value for the qualitative understanding of the phase transition.

Example 18.1: Ising model in one dimension

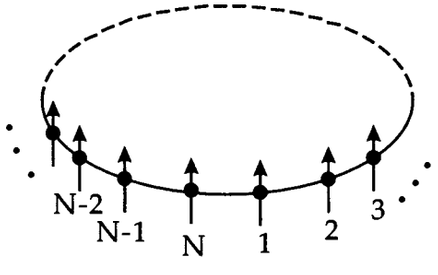


Figure 18.1. Closed one-dimensional Ising lattice.

The problem is essentially simplified if we postulate periodic boundary conditions; i.e., we connect the ends of the linear lattice to obtain a closed circle with N spins (see Figure 18.1). This corresponds, e.g., to periodic boundary conditions for a free particle in a box. The Hamiltonian, including an external magnetic field, reads

$$H_N(\sigma_1, \ldots, \sigma_N) = -I \sum_{n.n.} \sigma_i \sigma_k - \mu B \sum_{i=1}^{N} \sigma_i$$

if μ is the magnetic moment of the spins. Taking into account the infinite structure of the Ising chain, we can write the sums somewhat more symmetrically ($\sigma_{N+1} = \sigma_1$):

$$H_N(\sigma_1, \ldots, \sigma_N) = -I \sum_{i=1}^{N} \sigma_i \sigma_{i+1} - \frac{1}{2} \mu B \sum_{i=1}^{N} (\sigma_i + \sigma_{i+1})$$

Each state of the system is determined by the set $\sigma_1, \ldots, \sigma_i, \ldots, \sigma_N$, where σ_i can assume only the values $+1$ (spin up) or -1 (spin down). The partition function thus becomes

$$Z_N(B, T) = \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \exp\left\{\beta \sum_{i=1}^{N} \left[I\sigma_i\sigma_{i+1} + \frac{1}{2}\mu B(\sigma_i + \sigma_{i+1})\right]\right\} \tag{18.4}$$

Originally, Ising used a combinatoric method to evaluate the partition function. More simple and elegant, however, is the matrix method of Kramers and Wannier. We define an operator $\hat{P}$ in spin space (2 x 2 matrix) by the matrix elements

$$\left\langle \sigma_i \left| \hat{P} \right| \sigma_{i+1} \right\rangle = \exp\left\{\beta\left[I\sigma_i\sigma_{i+1} + \frac{1}{2}\mu B(\sigma_i + \sigma_{i+1})\right]\right\} \tag{18.5}$$

If a spin $\sigma_k = +1$ corresponds to the unit vector $\binom{1}{0}$ and a spin $\sigma_k = -1$ to the unit vector $\binom{0}{1}$, one immediately finds that the 2 x 2 matrix $\hat{P}$ must have the form

$$\hat{P} = \begin{pmatrix} \exp\{\beta(I + \mu B)\} & \exp\{-\beta I\} \\ \exp\{-\beta I\} & \exp\{\beta(I - \mu B)\} \end{pmatrix}$$

to fulfill Equation (18.5). One then obtains for Equation (18.4):

$$Z_N(B, T) = \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \left\langle \sigma_1 \left| \hat{P} \right| \sigma_2 \right\rangle \left\langle \sigma_2 \left| \hat{P} \right| \sigma_3 \right\rangle \cdots \left\langle \sigma_N \left| \hat{P} \right| \sigma_1 \right\rangle$$

Since the states $|\pm 1\rangle$ form a complete set, the closure relation $\sum_{\sigma=\pm 1} |\sigma\rangle \langle\sigma| = 1$ holds, and thus

$$Z_N(B, T) = \sum_{\sigma_1=\pm 1} \left\langle \sigma_1 \left| \hat{P}^N \right| \sigma_1 \right\rangle = \operatorname{Tr} \hat{P}^N \tag{18.6}$$

The trace can be readily calculated if $\hat{P}$ is transformed to diagonal form (this is always possible, since $\hat{P}$ is symmetric). Then the eigenvalues of $\hat{P}$ appear on the diagonal. These follow from the secular equation

$$\begin{vmatrix} \exp\{\beta(I + \mu B)\} - \lambda & \exp\{-\beta I\} \\ \exp\{-\beta I\} & \exp\{\beta(I - \mu B)\} - \lambda \end{vmatrix} = 0$$

$$\lambda^2 - 2\lambda \exp\{\beta I\} \cosh(\beta\mu B) + 2\sinh(2\beta I) = 0$$

The eigenvalues λ_1, λ_2 are the solutions of this equation:

$$\lambda_{1,2} = \exp\{\beta I\} \cosh(\beta\mu B) \pm \left[\exp\{-2\beta I\} + \exp\{2\beta I\} \sinh^2(\beta\mu B)\right]^{1/2}$$

Therefore, due to the invariance of the trace with respect to orthogonal transformations we obtain in Equation (18.6):

$$Z_N(B, T) = \operatorname{Tr} \hat{P}^N = \operatorname{Tr} \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}^N = \lambda_1^N + \lambda_2^N$$

Thus, the partition function is exactly calculated, as is the free energy:

$$F(N, B, T) = -kT \ln Z_N(B, T) = -kT \ln\left(\lambda_1^N + \lambda_2^N\right)$$

The thermodynamic properties of the system follow in a well-known way from the free energy by differentiation. For sake of brevity we introduce two useful abbreviations:

$$x = \beta\mu B \qquad y = \beta I$$

Then the eigenvalues λ_1 and λ_2 read

$$\lambda_{1,2}(x, y) = e^{y} \cosh x \pm \left[e^{-2y} + e^{2y} \sinh^2 x\right]^{1/2} \tag{18.7}$$

First we convince ourselves that the chain shows paramagnetic behavior if the interaction between the spins is switched off:

$$\begin{aligned} \lambda_{1,2}(x, 0) &= \cosh x \pm [1 + \sinh^2 x]^{1/2} \\ &= \begin{cases} 2 \cosh x \\ 0 \end{cases} \end{aligned} \tag{18.8}$$

The free energy

$$F(x, 0) = -NkT \ln\{2 \cosh x\}$$

agrees exactly with Equation (8.55). Especially interesting is the question of whether we obtain a spontaneous remanence magnetization in the chain without an external field (limit $x \to 0^+$), but with mutually interacting spins, as is necessary for ferromagnetic behavior. To answer this question we calculate the total magnetic moment:

$$\begin{aligned} D_z(N, B, T) &= -\left.\frac{\partial F}{\partial B}\right|_{N,T} \\ &= -\beta\mu \frac{\partial F}{\partial x} = \mu \frac{\partial}{\partial x} \ln\left\{\lambda_1^N + \lambda_2^N\right\}\Big|_{N,T} \\ &= N\mu \frac{\lambda_1^{N-1} \frac{\partial}{\partial x} \lambda_1 + \lambda_2^{N-1} \frac{\partial}{\partial x} \lambda_2}{\lambda_1^N + \lambda_2^N} \end{aligned} \tag{18.9}$$

With the help of Equation (18.7), we find

$$\begin{aligned} \frac{\partial}{\partial x} \lambda_{1,2} &= \frac{e^{y} \sinh x}{\left[e^{-2y} + e^{2y} \sinh^2 x\right]^{1/2}} \left([e^{-2y} + e^{2y} \sinh^2 x]^{1/2} \pm e^{y} \cosh x\right) \\ &= \frac{e^{y} \sinh x}{\left[e^{-2y} + e^{2y} \sinh^2 x\right]^{1/2}} (\pm\lambda_{1,2}) \end{aligned}$$

If we insert this into Equation (18.9), it follows that

$$D_z(x, y) = N\mu \frac{\sinh x}{[\exp\{-4y\} + \sinh^2 x]^{1/2}} \frac{\lambda_1^N - \lambda_2^N}{\lambda_1^N + \lambda_2^N} \tag{18.10}$$

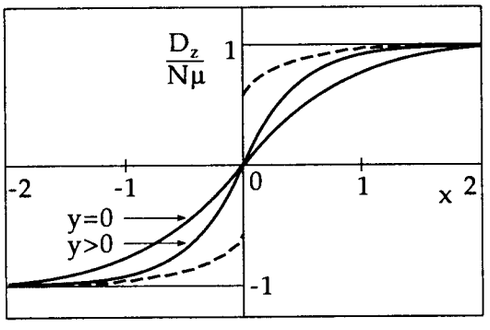


Figure 18.2. The function $D_z(x)$

One immediately realizes that always $\lim_{x \to 0} D_z(x, y) = 0$, since the sinh appears as a factor and the functions $\lambda_{1,2}(x, y)$ are always finite for $x \to 0$. For vanishing field, also, the magnetic moment of the chain vanishes.

The function $D_z(x, y)$ is shown in the Figure 18.2. For $y = 0$ it is

$$D_z(x, 0) = N\mu \tanh x$$

which corresponds to paramagnetic behavior. For $y > 0$, the spins can be more easily aligned by the external field, wherefore the curve becomes steeper; however, this is not sufficient to produce a finite magnetization without an external field.

If the interaction becomes very large in comparison to kT ($y \to \infty$), then

$$\lambda_{1,2}(x, y \gg 1) \approx \exp\{y \pm x\} \tag{18.11}$$

and therefore

$$D(x, y \gg 1) \approx N\mu \tanh Nx$$

The slope of the curve at $x = 0$ is directly given by the square of the number of spins. If this number is very large, for strong spin–spin interaction or for low temperatures ($T \to 0$), far smaller fields than in the paramagnetic case ($y = 0$) are sufficient to enforce the saturation magnetization, since in the paramagnetic case the slope of D_z is only linear in N. One therefore says that in the one-dimensional Ising model ($N \gg 1$) the phase transition to ferromagnetic behavior happens at $T_c = 0$.

We are now able to study the correlation of the spins more explicitly by calculating the mean numbers of up and down spins (N_+ and N_-, respectively), as well as the mean numbers of parallel and antiparallel nearest neighbors (N_{++}, N_{--}, and N_{+-}, respectively). To this end, we write

$$N_\pm = \frac{1}{2} N(1 \pm r) \qquad D_z = \mu(N_+ - N_-) = N\mu r$$

Since the magnetic moment D_z is known according to Equation (18.10), we obtain

$$N_\pm = \frac{1}{2} N \left(1 \pm \frac{\sinh x}{[\exp\{-4y\} + \sinh^2 x]^{1/2}} \frac{\lambda_1^N - \lambda_2^N}{\lambda_1^N + \lambda_2^N}\right)$$

In the limit $x \to 0$ ($B \to 0$, $T \neq 0$) it always holds that $N_\pm = \frac{1}{2} N$; i.e., there are as many up as down spins, while for $x \to \infty$ ($B \to \infty$, $T \neq \infty$), all spins are aligned: $N_+ = N$, $N_- = 0$. However, we will soon see that the interaction causes a positive correlation of the spins also in the limit $x \to 0$. This correlation can be measured by the average value of the quantity $\sigma_i\sigma_{i+1}$, i.e., the relative mutual orientation of nearest neighbors. If the spins $i, i + 1$ are aligned parallel (no matter whether up or down), $\sigma_i\sigma_{i+1} = +1$; if they are antiparallel, $\sigma_i\sigma_{i+1} = -1$. The relationship between the average value $\langle\sigma_i\sigma_{i+1}\rangle$ and the numbers N_{++}, N_{--}, and N_{+-} follows from a simple consideration, which we can perform even for a lattice with arbitrary coordination number q (q nearest neighbors). In a lattice with even coordination number q there are just $qN/2$ different pairs of nearest neighbors. If they are all oriented up ($N_{++} = qN/2$, $N_{--} = N_{+-} = 0$), or down ($N_{--} = qN/2$, $N_{++} = N_{+-} = 0$), it holds that $\sum_{n.n.} \sigma_i\sigma_k = qN/2$. However, if all nearest neighbors are antiparallel ($N_{+-} = qN/2$, $N_{++} = N_{--} = 0$), it holds that $\sum_{n.n.} \sigma_i\sigma_k = -qN/2$. Thus, the desired relationship obviously reads

$$\left\langle \sum_{n.n.} \sigma_i\sigma_k \right\rangle = N_{++} + N_{--} - N_{+-} \tag{18.12}$$

Here we can eliminate the numbers N_{++} and N_{--} with the help of N_+ and N_-. We first assume that each of the N_{++} mutually different pairs of parallel up spins contributes two up spins to N_+, and each of the N_{+-} antiparallel pairs contributes exactly one. The number of up spins would then be $2N_{++} + N_{+-}$. An analogous consideration holds, of course, for the down spins. Now there are in total $qN/2$ different pairs, wherefore we have counted each spin

q-fold with this consideration; i.e., the relations between N_{++}, N_{--} and N_+, N_- finally read

$$qN_+ = 2N_{++} + N_{+-}$$
$$qN_- = 2N_{--} + N_{+-}$$

If we eliminate N_{++} and N_{--} from Equation (18.12) with this result, all three numbers N_{++}, N_{--}, and N_{+-} can be calculated from the quantities N_+, N_-, and $\left\langle \sum_{n.n.} \sigma_i \sigma_k \right\rangle$ ($q = 2$):

$$\begin{aligned}
\frac{N_{+-}}{N} &= \frac{1}{2}\left(1 - \frac{1}{N}\left\langle \sum_{i=1}^{N} \sigma_i \sigma_{i+1} \right\rangle\right) \\
\frac{N_{++}}{N} &= \frac{N_+}{N} - \frac{1}{2}\frac{N_{+-}}{N} \\
\frac{N_{--}}{N} &= \frac{N_-}{N} - \frac{1}{2}\frac{N_{+-}}{N}
\end{aligned} \tag{18.13}$$

Finally, note that the average value $\langle \sigma_i \sigma_{i+1} \rangle$ for a certain pair does not depend on the index, due to the translational invariance of the lattice, and thus $N \langle \sigma_i \sigma_{i+1} \rangle = \left\langle \sum_{i=1}^{N} \sigma_i \sigma_{i+1} \right\rangle$. According to the general prescription for calculating mean values in statistical mechanics we have

$$\left\langle \sum_{i=1}^{N} \sigma_i \sigma_{i+1} \right\rangle =$$
$$\frac{\sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \left(\sum_{i=1}^{N} \sigma_i \sigma_{i+1}\right) \exp\left\{\beta \sum_{i=1}^{N} \left[I \sigma_i \sigma_{i+1} + \frac{1}{2}\mu B(\sigma_i + \sigma_{i+1})\right]\right\}}{\sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \exp\left\{\beta \sum_{i=1}^{N} \left[I \sigma_i \sigma_{i+1} + \frac{1}{2}\mu B(\sigma_i + \sigma_{i+1})\right]\right\}}$$

One immediately anticipates that this average must also follow by differentiation of $\ln Z$ with respect to the quantity $y = \beta I$, since the chain rule yields the sum $\sum_{i=1}^{N} \sigma_i \sigma_{i+1}$ as an additional factor in the nominator:

$$\left\langle \sum_{i=1}^{N} \sigma_i \sigma_{i+1} \right\rangle = \frac{\partial}{\partial y} \ln Z = \frac{\partial}{\partial y} \ln\left\{\lambda_1^N + \lambda_2^N\right\} \tag{18.14}$$

Here the derivative of $\lambda_{1,2}$ with respect to y is needed:

$$\begin{aligned}
\frac{\partial}{\partial y}\lambda_{1,2} &= e^y \cosh x \pm \frac{e^{2y}\sinh^2 x - e^{-2y}}{\left[e^{-2y} + e^{2y}\sinh^2 x\right]^{1/2}} \\
&= e^y \cosh x \pm [e^{2y}\sinh^2 \times + e^{-2y}]^{1/2} \\
&\quad \mp \frac{2e^{-2y}}{\left[e^{-2y} + e^{2y}\sinh^2 x\right]^{1/2}} \\
&= \lambda_{1,2} \mp \frac{2e^{-2y}}{\left[e^{-2y} + e^{2y}\sinh^2 x\right]^{1/2}}
\end{aligned}$$

Thus Equation (18.14) becomes

$$\left\langle \sum_{i=1}^{N} \sigma_i \sigma_{i+1} \right\rangle = N\left(1 - \frac{2e^{-2y}}{\left[e^{-2y} + e^{2y}\sinh^2 x\right]^{1/2}} \frac{\lambda_1^{N-1} - \lambda_2^{N-1}}{\lambda_1^N + \lambda_2^N}\right)$$

According to Equation (18.13), the number of antiparallel pairs is

$$\frac{N_{+-}}{N} = \frac{e^{-3y}}{[e^{-4y} + \sinh^2 x]^{1/2}} \frac{\lambda_1^{N-1} - \lambda_2^{N-1}}{\lambda_1^N + \lambda_2^N} \tag{18.15}$$

If the interaction is switched off ($y = 0$) (i.e., in the paramagnetic case) this becomes, with Equation (18.8):

$$\frac{N_{+-}}{N}(y = 0) = \frac{1}{2}\cosh^{-2} x \tag{18.16}$$

For $x = 0$, therefore, $N_{+-} = \frac{1}{2}N$, and due to $N_+ = N_- = \frac{1}{2}N$, it follows from Equation (18.12) that $N_{++} = N_{--} = \frac{1}{4}N$; i.e., half of all pairs are antiparallel, one-quarter are parallel up, and one-quarter are parallel down. If a magnetic field is turned on, the number of antiparallel pairs decreases rapidly according to Equation (18.16), and correspondingly, the number N_{++} increases.

If we consider, on the other hand, the case of strong interaction between the spins ($y \gg 1$), Equation (18.15) becomes, with the help of Equation (18.11):

$$\frac{N_{+-}}{N}(y \gg 1) \approx e^{-4y} \frac{\sinh(N-1)x}{\sinh x \cosh Nx}$$

The number of antiparallel pairs is thus exponentially suppressed with increasing interaction; i.e., a block structure is enforced in the chain, where the spins in each block are aligned parallel. Since there are equal numbers of up and down blocks for vanishing magnetic field, the total magnetization vanishes.

Example 18.2: Ising model in the mean-field approximation

In the mean-field approximation of the Ising model, it is assumed that each spin does not interact directly with its nearest neighbors, but with a mean field, which follows from the mean orientation of the neighboring spins. One substitutes the approximation $-Iq\,\langle\sigma\rangle \sum_i \sigma_i$ for the exact interaction $-I \sum_{n.n.} \sigma_i\sigma_k$, where the q nearest neighbors are replaced by the mean spin $q\,\langle\sigma\rangle$. To investigate this approximation more closely we consider the identity

$$\sigma_i\sigma_k = \sigma_i\,\langle\sigma_k\rangle + \langle\sigma_i\rangle\,\sigma_k - \langle\sigma_i\rangle\,\langle\sigma_k\rangle + (\sigma_i - \langle\sigma_i\rangle)(\sigma_k - \langle\sigma_k\rangle) \tag{18.17}$$

where the average values $\langle\sigma_i\rangle$ do not depend on the index i due to translational invariance. The exact interaction thus reads

$$\begin{aligned} &H_I(\sigma_1, \ldots, \sigma_N) \\ &= -I \sum_{n.n.} [\sigma_i\,\langle\sigma\rangle + \langle\sigma\rangle\,\sigma_k - \langle\sigma\rangle^2 \\ &\quad + (\sigma_i - \langle\sigma\rangle)(\sigma_k - \langle\sigma\rangle)] \end{aligned} \tag{18.18}$$

Since each central spin σ_i with neighbor σ_k is also a neighboring spin of the central spin σ_k, the values of the first two sums are identical. On the other hand, there are exactly $qN/2$ different pairs: $q/2$ different pairs belong to each spin σ_i, $i = 1, \ldots, N$, $q/2$. Thus Equation (18.18)

becomes

$$H_I(\sigma_1, \ldots, \sigma_N) = -Iq\,\langle\sigma\rangle \sum_{i=1}^{N} \sigma_i + I\frac{q}{2} N\,\langle\sigma\rangle^2 - I\sum_{n.n.} (\sigma_i - \langle\sigma\rangle)(\sigma_k - \langle\sigma\rangle)$$

So far this expression is still exact. The first term just has the form mentioned in the beginning, while the second term represents a constant expectation value which no longer depends on a special orientation of the spins. Finally, the last term contains the spin fluctuations, i.e., the deviations of a certain spin from its mean orientation. The mean-field approximation corresponds to neglecting this term. Thus we have the effective interaction

$$H_I^{m.f.}(\sigma_1, \ldots, \sigma_N) = -Iq\,\langle\sigma\rangle \sum_{i=1}^{N} \sigma_i + I\frac{q}{2} N\,\langle\sigma\rangle^2 \tag{18.19}$$

If one takes the expectation value

$$U = \left\langle H_I^{m.f.} \right\rangle = -IqN\,\langle\sigma\rangle^2 + I\frac{q}{2} N\,\langle\sigma\rangle^2 = -I\frac{q}{2} N\,\langle\sigma\rangle^2 \tag{18.20}$$

one finds for complete alignment, $\langle\sigma\rangle = 1$, the value $U = -\frac{1}{2}qNI$, as it should be, since each of the $qN/2$ different pairs contributes the amount $-I$. Since the Hamiltonian (18.19) contains the statistical average $\langle\sigma\rangle$, which in principle has to be calculated first, we obtain a self-consistency problem for determining $\langle\sigma\rangle$.

The average of the magnetic dipole moment is

$$D = \mu \left\langle \sum_{i=1}^{N} \sigma_i \right\rangle = N\mu\,\langle\sigma\rangle \tag{18.21}$$

if each spin has the magnetic moment μ. This is equivalent to determining the magnetic moment from the general formula

$$D = -\frac{\partial}{\partial B} F(N, B, T, \langle\sigma\rangle)\Big|_{N,T,\langle\sigma\rangle} \tag{18.22}$$

where the free energy itself depends on the average $\langle\sigma\rangle$. The identity of Equations (18.21) and (18.22) is most easily anticipated if one inserts the definition $Z = \sum_{\sigma_1=\pm1} \cdots \sum_{\sigma_N=\pm1} \exp\{-\beta H\}$ with the energy $H^{m.f.} = H_I^{m.f.} - \mu B \sum_{i=1}^{N} \sigma_i$ ($H_I^{m.f.}$ from Equation (18.19)) into $F = -kT \ln Z(N, B, T, \langle\sigma\rangle)$ and performs the differentiation (18.22).

If one combines Equations (18.21) and (18.22), one obtains an implicit equation for $\langle\sigma\rangle$. By the way, in Equation (18.22) one differentiates at constant $\langle\sigma\rangle$, although this mean value depends on the thermodynamic variables N, B, and T. The only reason for this is to set the general prescription (18.22) in accordance with the physically sensible "definition" of the magnetic dipole moment (18.21).

The complete Hamiltonian with an external magnetic field in mean-field approximation is, as mentioned above,

$$H^{m.f.}(\sigma_1, \ldots, \sigma_N) = I\frac{q}{2} N\,\langle\sigma\rangle^2 - \mu(B^{m.f.} + B) \sum_{i=1}^{N} \sigma_i \tag{18.23}$$

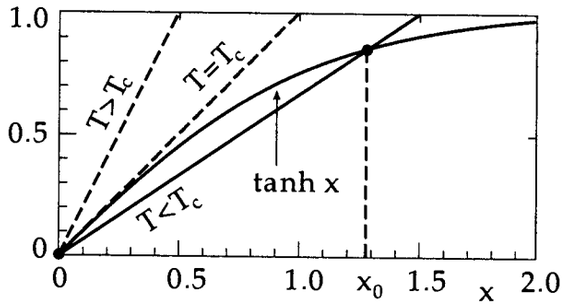


Figure 18.3. Concerning the solution of Equation (18.26), $B = 0$.

with the additional mean magnetic field caused by the spins

$$B^{m.f.} = q \frac{I \langle \sigma \rangle}{\mu}$$

Formally, $H^{m.f.}$ is identical up to the constant term with the corresponding paramagnetic expression (8.41). In particular, Equation (18.23) is a sum of one-particle Hamiltonians, wherefore the evaluation is considerably simplified. The partition function is

$$\begin{aligned} Z(N, T, B, \langle \sigma \rangle) &= \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} \exp\left\{ -\frac{1}{2} \beta q N I \langle \sigma \rangle^2 \right\} \\ &\quad \times \exp\left\{ \beta \mu (B^{m.f.} + B) \sum_{i=1}^{N} \sigma_i \right\} \\ &= \exp\left\{ -\frac{1}{2} \beta q N I \langle \sigma \rangle^2 \right\} \left[\sum_{\sigma = \pm 1} \exp\left\{ \beta \mu (B^{m.f.} + B) \sigma \right\} \right]^N \\ &= \exp\left\{ -\frac{1}{2} \beta q N I \langle \sigma \rangle^2 \right\} \left[2 \cosh\left\{ \beta \mu (B^{m.f.} + B) \right\} \right]^N \end{aligned}$$

with the corresponding free energy

$$F(N, T, B, \langle \sigma \rangle) = \frac{1}{2} q N I \langle \sigma \rangle^2 - N k T \ln\left[2 \cosh\left\{ \beta \mu (B^{m.f.} + B) \right\} \right]$$

From this we have according to Equation (18.22) the following equation for $\langle \sigma \rangle$:

$$\langle \sigma \rangle = \tanh\left\{ \beta \mu \left(\frac{qI}{\mu} \langle \sigma \rangle + B \right) \right\} \tag{18.24}$$

To put this equation into a convenient form we substitute the new variable

$$x = \beta q I \langle \sigma \rangle + \beta \mu B \tag{18.25}$$

and obtain

$$\frac{1}{\beta q I} (x - \beta \mu B) = \tanh x, \qquad \text{or} \qquad \frac{1}{\beta q I} x = \tanh x \qquad \text{for} \qquad B = 0 \tag{18.26}$$

The determination of $\langle \sigma \rangle$ from Equation (18.24) is of course identical with the determination of x from Equation (18.26). The solutions x of Equation (18.26) are the intersections of a

straight line $ax + b$ with the function $\tanh x$. We first investigate the particularly interesting case of a vanishing magnetic field ($B = 0$). The straight line crosses the origin $x = 0$ and has the slope $1/(\beta q I)$ (Figure 18.3).

If we set

$$T_c = \frac{qI}{k}\frac{T}{T_c} = \frac{1}{\beta q I} \tag{18.27}$$

one realizes that for $T > T_c$ only the trivial solution $x = 0$ and thus $\langle\sigma\rangle = 0$ exists. The spins are completely statistically oriented for $T > T_c$ without an external magnetic field.

For $T = T_c$, the slope of the straight line is just 1, as that of $\tanh x$ at $x = 0$.

For $T < T_c$, there is also a nontrivial solution x_0 besides $x = 0$. This corresponds to a nonvanishing orientation $\langle\sigma\rangle \neq 0$, and thus to a spontaneous magnetization of the lattice. Hence, there really occurs a phase transition to ferromagnetic behavior at the critical temperature T_c. However, this is also the case for $q = 2$, although we know from the exact solution (preceding example) that there is no phase transition in this case. Thus, the mean-field approximation can only be good for larger q values (e.g., $q = 12$ for a cubic face-centered lattice). Near $T = T_c$ one can find an approximate solution of Equation (18.26) by expanding $\tanh x$ with respect to small x ($B = 0$):

$$\frac{T}{T_c}x = x - \frac{1}{3}x^3 + \cdots$$

or

$$x_0 = \left[3\left(1 - \frac{T}{T_c}\right)\right]^{1/2} \qquad \text{for} \qquad T \leq T_c \tag{18.28}$$

Since $x_0 = \langle\sigma\rangle\, T_c/T$ the critical index of the phase transition for the order parameter $\langle\sigma\rangle$ is exactly $\beta = \frac{1}{2}$, which is at least in the vicinity of the experimental value $\beta \approx 0.33$.

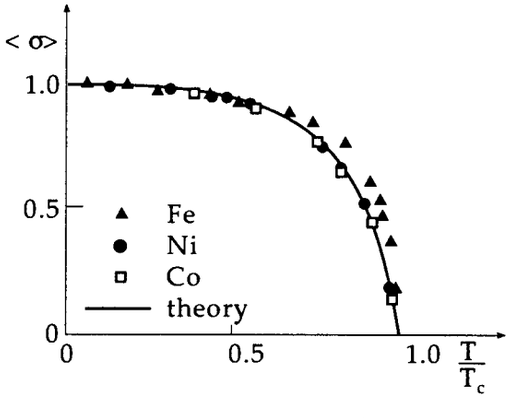


Figure 18.4. Order parameter $\langle\sigma\rangle$ of the Ising model.

If one plots the values for x_0 or $\langle\sigma\rangle$ versus the reduced temperature T/T_c, one obtains the typical ferromagnetic behavior of spontaneous magnetization (cf. Figure 17.12). For comparison, experimental data is also shown in Figure 18.4. For low temperatures ($T \to 0$), the slope of the straight line is very small, and the intersection is at large x values. Then one can expand $\tanh x$ for large x, and Equation (18.26) becomes

$$\frac{T}{T_c}x = 1 - 2\exp\{-2x\} + \cdots$$

This equation can be iteratively solved. The zeroth approximation is $x_0 = T_c/T$. If one inserts this on the right-hand side, one obtains the first approximation

$$\langle\sigma\rangle = \frac{T}{T_c}x_0 \approx 1 - 2\exp\left\{-2\frac{T_c}{T}\right\} \qquad \text{for} \qquad \frac{T}{T_c} \ll 1$$

For low temperatures, this model predicts an exponentially small deviation from the saturation magnetization $\langle\sigma\rangle = 1$. However, experimental precision measurements yield

$$\langle\sigma\rangle \approx 1 - \text{const.}T^{3/2}$$

This is a first hint of the insufficiency of the mean-field approximation or of the Ising model. Obviously, in reality the system can be far more easily excited at low temperatures than is

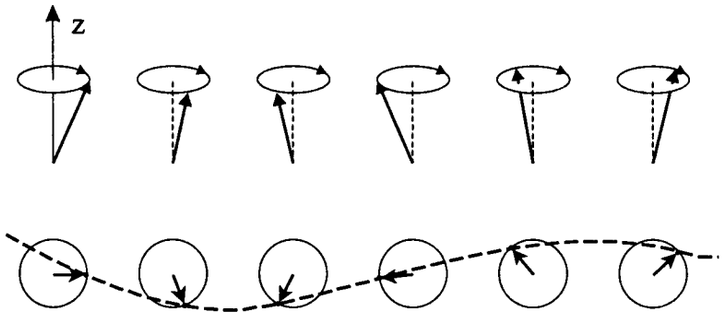


Figure 18.5. Collective precession of the spins (spin–wave).

predicted by our model, because the deviations of the saturation magnetization grow like $T^{3/2}$. The reason is that the Ising model takes only the z-components of the spin vectors into account. However, at low temperatures a complete spin flip rapidly becomes very improbable ($\propto \exp\{-\Delta\epsilon/kT\}$). In the classical interpretation the spin vectors can also perform a precession around the z-axis. Thus, collective excitations of the precession can occur (see Figure 18.5), the quanta of which are called *magnons* (in analogy to the phonons of the lattice oscillations). If the phase shift of the precession is constant between single spins, spin waves are formed. Since magnons have an energy–momentum relation $\epsilon \propto p$, like phonons, their excitation leads to a $T^{3/2}$ behavior, as in the Debye model of the lattice oscillations.

The internal energy of the Ising lattice can be calculated from Equations (18.20) or (18.23). For $B = 0$ it is

$$U_0 = -\frac{1}{2} qNI \langle\sigma\rangle^2 \tag{18.29}$$

Thus, for $B = 0$ the specific heat of the system is given by

$$C_0 = -qNI \langle\sigma\rangle \frac{d\langle\sigma\rangle}{dT} = -NkT_c \langle\sigma\rangle \frac{d\langle\sigma\rangle}{dT}$$

where Equation (18.27) was used. The derivative of $\langle\sigma\rangle$ can be calculated from Equation (18.26). It is

$$\langle\sigma\rangle = \tanh\left\{\frac{T_c}{T}\langle\sigma\rangle\right\}$$

and therefore

$$\begin{aligned}\frac{d\langle\sigma\rangle}{dT} &= \left(1 - \tanh^2\left\{\frac{T_c}{T}\langle\sigma\rangle\right\}\right)\left(-\frac{T_c\langle\sigma\rangle}{T^2} + \frac{T_c}{T}\frac{d\langle\sigma\rangle}{dT}\right) \\ &= \left(1 - \langle\sigma\rangle^2\right)\left(-\frac{T_c\langle\sigma\rangle}{T^2} + \frac{T_c}{T}\frac{d\langle\sigma\rangle}{dT}\right)\end{aligned} \tag{18.30}$$

If one solves Equation (18.30) for $d\langle\sigma\rangle/dT$, one gets

$$\frac{d\langle\sigma\rangle}{dT} = \frac{\left(1 - \langle\sigma\rangle^2\right)\frac{T_c\langle\sigma\rangle}{T^2}}{\left(1 - \langle\sigma\rangle^2\right)\frac{T_c}{T} - 1} \tag{18.31}$$

Especially interesting, of course, is the behavior near $T = T_c$. The internal energy increases with decreasing order parameter $\langle\sigma\rangle$, until it vanishes at the critical temperature $T = T_c$, where $\langle\sigma\rangle = 0$. For $T > T_c$, $\langle\sigma\rangle = 0$ and as well $U_0 = 0$. Since $\langle\sigma\rangle$ shows a kink at

$T = T_c$, the specific heat has to be discontinuous. Above T_c it has to be $C_0 = 0$, since also $U_0 = 0$. For $T < T_c$ it is

$$C_0(T) = -Nk \frac{T_c}{T} \langle\sigma\rangle^2 \frac{1 - \langle\sigma\rangle^2}{1 - \langle\sigma\rangle^2 - \frac{T}{T_c}} \tag{18.32}$$

Near the critical temperature we may use

$$\langle\sigma\rangle^2 = \left(\frac{T}{T_c}\right)^2 3\left(1 - \frac{T}{T_c}\right)$$

as an approximation (cf. Equation (18.28)). Hence

$$C_0(T \leq T_c) \approx -Nk\left(\frac{T}{T_c}\right) 3\left(1 - \frac{T}{T_c}\right) \frac{1 - 3\left(\frac{T}{T_c}\right)^2 + 3\left(\frac{T}{T_c}\right)^3}{\left(1 - \frac{T}{T_c}\right)\left(1 - 3\left(\frac{T}{T_c}\right)^2\right)}$$

$$\approx 3Nk \frac{T}{T_c} \frac{1 - 3\left(\frac{T}{T_c}\right)^2 + 3\left(\frac{T}{T_c}\right)^3}{3\left(\frac{T}{T_c}\right)^2 - 1}$$

In the limit $T \to T_c$ we thus have

$$C_0(T_c) = \frac{3}{2} Nk$$

The specific heat jumps by $\frac{3}{2} Nk$ at $T = T_c$ (Figure 18.6).

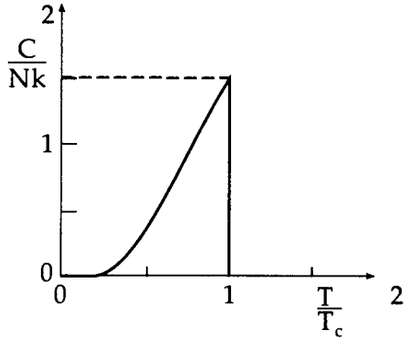


Figure 18.6. Specific heat in the Ising model.

Let us briefly examine the case $B \neq 0$. Since the straight lines $ax + b$ are now shifted to the right, there always exist nontrivial solutions $\langle\sigma\rangle \neq 0$ of Equation (18.26) (cf. Figure 18.7).

If we restrict ourselves to high temperatures $T \gg T_c$, $\beta\mu B \ll 1$ and the slopes of the straight lines become very large. The intersections x_0 are then very near to $x = 0$, and we may again expand $\tanh x$ in Equation (18.26) in terms of small x values

$$\frac{T}{T_c}(x - \beta\mu B) \approx x$$

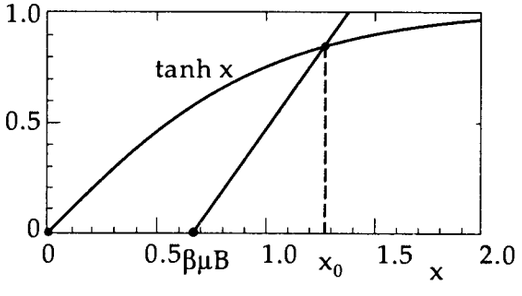


Figure 18.7. Concerning the solution of Equation (18.26), $B \neq 0$.

or, with Equation (18.25),

$$\langle\sigma\rangle = \frac{\mu B}{k(T - T_c)} \qquad \text{for} \quad T \gg T_c$$

The total magnetic moment thus has the form

$$D = N\mu\langle\sigma\rangle = \frac{N\mu^2 B}{k(T - T_c)} \qquad \text{for} \quad T \gg T_c$$

and the susceptibility obeys the Curie–Weiss law,

$$\chi = \frac{D}{B} = \frac{N\mu^2/k}{T - T_c} \qquad \text{for} \quad T \gg T_c$$

It is very useful to study the mean-field approximation again from a different point of view. To this end, we use the notations of Example 18.1. In particular, let N_+, and N_- be the numbers of up and down spins, and N_{++}, N_{--}, and N_{+-} the numbers of pairs with parallel up and down spins, and with antiparallel spins, respectively.

With

$$N_\pm = \frac{N}{2}(1 \pm r)$$
$$D = N\mu r \tag{18.33}$$

it follows that $r = \langle\sigma\rangle$. Now we can readily calculate (microcanonically) the number of states for a given number of up and down spins,

$$\Omega = \frac{N!}{N_+!N_-!} \qquad N = N_+ + N_- \tag{18.34}$$

There are just $N!$ ways to permutate the spins; however, $N_\pm!$ permutations of the spins with equal orientation do not yield a new situation. Therefore, the entropy is, with Stirling's formula $\ln N! \approx N \ln N - N$:

$$S = k \ln \Omega = -k\left(N_+ \ln \frac{N_+}{N} + N_- \ln \frac{N_-}{N}\right)$$

or with Equation (18.33):

$$S = -kN\left(\frac{1}{2}(1+r)\ln\left\{\frac{1}{2}(1+r)\right\} + \frac{1}{2}(1-r)\ln\left\{\frac{1}{2}(1-r)\right\}\right) \tag{18.35}$$

The total energy (18.29) can be expressed in terms of the numbers N_{++}, N_{--}, and N_{+-}, where parallel pairs contribute the energy $-I$ and antiparallel pairs the energy $+I$,

$$U = -I(N_{++} + N_{--} - N_{+-}) \tag{18.36}$$

We now try to relate the numbers N_{++}, N_{--}, and N_{+-} to N_+ and N_- with the help of a plausible approximation. Of course, this cannot be exact, since we already know regarding Equation (18.12) of the last example that with the help of N_+ and N_- only two of these numbers can be eliminated.

We take $p_+ = N_+/N$ as the probability of finding an up spin at an arbitrary lattice site, and $p_- = N_-/N$ as the probability of finding a down spin. In total, there are $\frac{1}{2}qN$ different pairs. If we now assume the probability of finding two neighboring up spins to be proportional to p_+^2, the mean number of parallel up pairs should be $\overline{N_{++}} = \frac{1}{2}qNp_+^2$, and analogously, the mean number of parallel down pairs $\overline{N_{--}} = \frac{1}{2}qNp_-^2$. It necessarily follows that $\overline{N_{+-}} = \frac{1}{2}qN(1 - p_+^2 - p_-^2)$, since always $\overline{N_{++}} + \overline{N_{--}} + \overline{N_{+-}} = \frac{1}{2}qN$.

Thus, the following scheme is obtained:

$$\overline{N_{++}} = \frac{q}{2}Np_+^2 = \frac{q}{8}N(1+r)^2$$
$$\overline{N_{--}} = \frac{q}{2}Np_-^2 = \frac{q}{8}N(1-r)^2$$
$$\overline{N_{+-}} = \frac{q}{2}N\left(1 - p_-^2 - p_+^2\right) = \frac{q}{4}N(1-r^2) \tag{18.37}$$

Also the total energy (18.36) can now be expressed in terms of the order parameter r, if we substitute the numbers N_{++}, N_{--}, and N_{+-} by their averages (18.37):

$$U = -\frac{q}{2}NIr^2 \tag{18.38}$$

which agrees with Equation (18.20). From Equations (18.38) and (18.35) the free energy follows as a function of r,

$$\begin{aligned} F &= U - TS \\ &= -\frac{1}{2}qNIr^2 + NkT\left[\frac{1}{2}(1+r)\ln\left\{\frac{1}{2}(1+r)\right\}\right. \\ &\quad \left. + \frac{1}{2}(1-r)\ln\left\{\frac{1}{2}(1-r)\right\}\right] \end{aligned}$$

In thermodynamic equilibrium F assumes a minimum. The most probable value of r is thus determined by

$$\frac{\partial F}{\partial r} = 0$$

This condition,

$$qNIr = \frac{1}{2}NkT\ln\frac{1+r}{1-r}$$

is just equivalent to Equation (18.25), if we use $\left[\ln\frac{1+r}{1-r}\right]^{1/2} = \operatorname{arctanh} x$,

$$\tanh\left(\frac{qI}{kT}r\right) = r$$

The mean-field approximation can therefore be interpreted in a very illustrative way by the approximation scheme (18.37). This scheme just corresponds to averaging over all configurations the lattice can assume, where each configuration has the same probability. This is, of course, not correct in a strict sense, since in the vicinity of up spins, more up spins gather. These correlations are neglected in Equation (18.37).

Exercise 18.3: Heisenberg model in the mean-field approximation

Investigate the following generalized Hamiltonian:

$$\hat{H} = -\sum_{l,m=1}^{N} I_{lm}\hat{\vec{s}}_l \cdot \hat{\vec{s}}_m - g\mu_B\vec{H}\cdot\sum_l \hat{\vec{s}}_l \qquad \textbf{(18.39)}$$

in the mean-field approximation. Here the I_{lm} are the exchange integrals, $\hat{\vec{s}}_l$ the spin operators (spin quantum number s), and $\vec{H}$ is the external magnetic field strength. Show that the mean–field approximation yields the same results for the Heisenberg model as for the corresponding Ising model. Derive an equation to calculate the mean field, and determine the critical temperature of the phase transition in the field-free case. Calculate the paramagnetic susceptibility in the limit $T \gg T_c$. What changes, if the exchange integrals become negative (antiferromagnetism)?

Solution:

To get $\hat{H}$ in the mean-field approximation, one uses an identity which is analogous to Equation (18.17):

$$\vec{s}_l \cdot \vec{s}_m = \vec{s}_l \cdot \langle\vec{s}_m\rangle + \langle\vec{s}_l\rangle \cdot \vec{s}_m - \langle\vec{s}_l\rangle \cdot \langle\vec{s}_m\rangle + (\vec{s}_l - \langle\vec{s}_l\rangle)\cdot(\vec{s}_m - \langle\vec{s}_m\rangle)$$

Neglecting the fluctuations (the last term), one obtains

$$\hat{H}^{m.f.} = -\sum_{l=1}^{N} \left\{ 2 \sum_{m=1}^{N} I_{lm} \langle \vec{s}_m \rangle + g\mu_B \vec{H} \right\} \cdot \vec{s}_l + \sum_{l,m=1}^{N} I_{lm} \langle \vec{s}_l \rangle \cdot \langle \vec{s}_m \rangle \tag{18.40}$$

Since the expectation values of the x- and y-components of the spin vectors vanish (magnetic field in z-direction), Equation (18.40) is completely equivalent to the mean-field approximation of the Ising model, where *a priori* only the z-components of the spins are considered. However, when we compare both models we have to consider that the I_{lm} are larger by a factor of 2 than the value I of the preceding example. One immediately anticipates this, if one takes into account the expectation value of the energy in the field-free case and assumes that the I_{lm} are zero except for nearest neighbors, and that for these they all have the same value I',

$$U_0(H=0) = \left\langle \hat{H}^{m.f.}(H=0) \right\rangle = -\sum_{l,m=1}^{N} I_{lm} \langle \vec{s}_l \rangle \cdot \langle \vec{s}_l \rangle$$

$$= -\langle s_z \rangle^2 \sum_{l=1}^{N} \sum_{m=n.n.} I_{lm} = -NqI' \langle s_z \rangle^2$$

where only the z-components $\langle s_{lz} \rangle$ of the spin operators have nonvanishing averages, which furthermore do not depend on the indices l or m, respectively. Especially for $s = \frac{1}{2}, s_z = \pm\frac{1}{2}$, or $\langle s_z \rangle = \frac{1}{2} \langle \sigma \rangle$, one realizes by comparison with Equation (18.20) that here $I'/2$ has to be identified with I.

The mean magnetic field which acts on the spin l is given by

$$g\mu_B \vec{H}_l^{m.f.} = 2 \sum_{m} I_{lm} \langle s_m \rangle + g\mu_B \vec{H}$$

Then the Hamiltonian simply reads

$$\hat{H}^{m.f.} = -g\mu_B \sum_{l=1}^{N} \vec{H}_l^{m.f.} \cdot \vec{s}_l + E_0 \qquad \text{with} \quad E_0 = \sum_{l,m=1}^{N} I_{lm} \langle \vec{s}_l \rangle \cdot \langle \vec{s}_m \rangle$$

From the considerations in Chapter 8, we know how the spin l behaves in the mean field $H_l^{m.f.}$. For instance, its mean magnetic moment is given by (we only consider the particular spin no. l):

$$\langle D_{lz} \rangle = g\mu_B s B_s(\beta g \mu_B H_l^{m.f.} s)$$

where $B_s(x)$ is the Brillouin function for index s. On the other hand, it holds that $D_{lz} = g\mu_B \langle s_{lz} \rangle$, and we obtain the self-consistency equations

$$\langle s_{lz} \rangle = s B_s(\beta g \mu_B H_l^{m.f.} s) \qquad l = 1, \ldots, N$$

$$= s B_s \left\{ s\beta \left(2 \sum_{m} I_{lm} \langle s_{mz} \rangle + g\mu_B H \right) \right\} \tag{18.41}$$

for the determination of the expectation values $\langle s_{lz} \rangle$. Equation (18.41) is now in general a system of N equations for determining the N expectation values. The advantage of this general formulation is that the antiferromagnetic behavior also can be investigated. In this case, the spins tend to orientate themselves antiparallel, due to $I_{lm} < 0$. The mean orientation $\langle s_{lz} \rangle$ of the spins will therefore change sign from lattice site to lattice site. On the other hand,

the contributions $|\langle s_{lz}\rangle|$ should no longer depend on the lattice position l, since the lattice is translationally invariant and looks the same when viewed from any position l. Thus we can set

$$\langle s_{lz}\rangle = C_l|\langle s_z\rangle| \qquad \begin{cases} C_l = 1 & \text{Ferromagnets} \\ C_l = \pm 1 & \text{Antiferromagnets} \end{cases}$$

Now only one equation remains which determines the absolute value of the mean orientation,

$$|\langle s_z\rangle| = sB_s\left\{s\beta\left(2\sum_m C_m I_{lm}|\langle s_z\rangle| + g\mu_B H\right)\right\} \tag{18.42}$$

The expression $\sum_m C_m I_{lm}$ also can no longer depend on the index l. This equation for $|\langle s_z\rangle|$ is, for $s = \frac{1}{2}$, completely equivalent to Equation (18.24), since in this case it holds that $B_{1/2} = \tanh x$. If we substitute

$$x = 2s\beta\sum_m C_m I_{lm}|\langle s_z\rangle| + \beta g\mu_B Hs$$

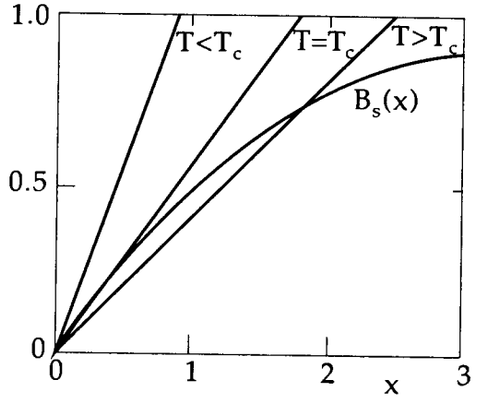


Figure 18.8. Concerning the solution of Equation (18.43).

Equation (18.42) becomes

$$\left[2s\beta\sum_m C_m I_{lm}\right]^{-1}(x - \beta g\mu_B Hs) = sB_s(x) \tag{18.43}$$

The critical temperature for $H = 0$ is determined analogously to the preceding example. The slope of the Brillouin function at $x = 0$ is given by Equation (8.51). The critical temperature thus follows from

$$\left[2s\beta\sum_m C_m I_{lm}\right]^{-1} x \approx \frac{1}{3}(s+1)x + \cdots$$

i.e.,

$$kT_c = \frac{2}{3}s(s+1)\sum_m C_m I_{lm} \tag{18.44}$$

In the case of a ferromagnetic nearest neighbor interaction, we have to set $\sum_m C_m I_{lm} = qI'$, and for $s = \frac{1}{2}$ it follows that $kT_c(s = \frac{1}{2}) = \frac{1}{2}qI'$, which agrees with Equation (18.27), because $\frac{1}{2}I' = I$.

If one plots the spontaneous magnetization determined from Equation (18.43) for different values of s, analogously to Figure 18.4, comparison with experiment yields the conclusion that the ferromagnetic behavior is indeed due to spins $s = \frac{1}{2}$ (Figure 18.9). However, this does not hold for some ferromagnetics of the $4f$ electron series, e.g., gadolinium. In these elements the orbit angular momenta may also contribute to the magnetic moment.

Finally we have to determine the susceptibility in the paramagnetic phase. For $T \gg T_c$, the mean orientation $\langle s_{lz}\rangle$ also points in field direction in the antiferromagnetic case $I_{lm} < 0$, and the coefficients C_m can be generally set to $C_m = 1$.

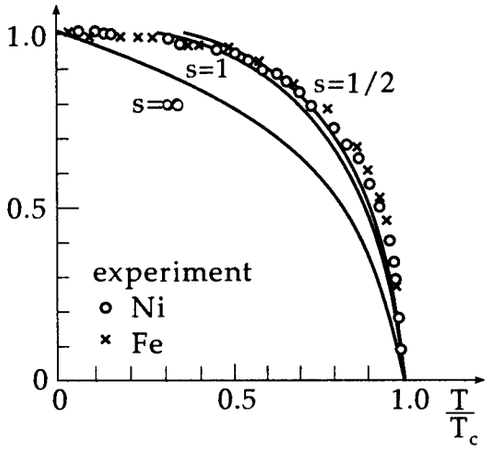


Figure 18.9. Spontaneous magnetization.

For $T \to \infty$, the intersection x_0 is again at $x \approx 0$ and one may expand the Brillouin function in (18.43) in terms of small x:

$$\left[2s\beta \sum_m I_{lm}\right]^{-1} (x - \beta g \mu_B H s) \approx \frac{1}{3}(s+1)x$$

or, according to Equation (18.42),

$$\langle s_z \rangle = \frac{\beta}{3} s(s+1)\left(2\sum_m I_{lm} \langle s_z \rangle + g\mu_B H\right)$$

If one solves this for $\langle s_z \rangle$, one obtains

$$\langle s_z \rangle = \frac{\frac{1}{3}s(s+1)g\mu_B H}{k(T - T_c')} \qquad \text{with} \quad kT_c' = \frac{2}{3}s(s+1)\sum_m I_{lm}$$

Therefore, the susceptibility is

$$\chi = \frac{D_z}{H} = \frac{Ng\mu_B \langle s_z \rangle}{H} = \frac{C}{T - T_c'}$$

with

$$C = \frac{g^2 \mu_B^2 N s(s+1)}{3k}$$

In the ferromagnetic case T_c' agrees with the temperature of the phase transition (18.44), $T_c' = T_c$.

In the antiferromagnetic case, however, $T_c' < 0$ because $I_{lm} < 0$ and $T_c' \neq T_c$, as the comparison with (18.44) shows. We now realize that in Equation (17.30) the parameter Θ is $-T_c'$.

Example 18.4: Order–disorder phase transitions in the Ising model

In this Example we want to show that the consequences of the Ising model can be readily applied to other phase transitions. We will use the mean-field approximation as it was presented in the last Examples, in the formulation of Bragg and Williams. As a model system we will consider an alloy of type AB with N_A A-atoms and N_B B-atoms, i.e., with the concentrations $x_A = N_A/N$ and $x_B = N_B/N$. Below the critical temperature, the atoms are ordered in two separate sublattices, which we call lattice a and lattice b. Above T_c, the atoms are statistically distributed over both sublattices (cf. Chapter 17). If we denote the number of A-atoms on lattice a by $\begin{bmatrix} A \\ a \end{bmatrix}$, that of A-atoms on lattice b by $\begin{bmatrix} A \\ b \end{bmatrix}$, and analogously for the B-atoms, we can write

$$\begin{bmatrix} A \\ a \end{bmatrix} = \frac{N}{2}x_A(1+r) \qquad \begin{bmatrix} B \\ a \end{bmatrix} = \frac{N}{2}(x_B - x_A r)$$

$$\begin{bmatrix} A \\ b \end{bmatrix} = \frac{N}{2}x_A(1-r) \qquad \begin{bmatrix} B \\ b \end{bmatrix} = \frac{N}{2}(x_B + x_A r) \qquad \textbf{(18.45)}$$

The order parameter r has an analogous meaning to the case of the spin lattice. If $r = 1$, all A-atoms are located in lattice a and none are in lattice b; all further free positions have to occupied with B-atoms. The second line in Equation (18.45) follows from the fact that lattices a and b each contain $\frac{1}{2}N$ positions, so that $\begin{bmatrix} A \\ a \end{bmatrix} + \begin{bmatrix} B \\ a \end{bmatrix} = \frac{1}{2}N$ and $\begin{bmatrix} A \\ b \end{bmatrix} + \begin{bmatrix} B \\ b \end{bmatrix} = \frac{1}{2}N$. The atoms of both lattices will now interact. The nearest neighbor of an atom on lattice a is always an atom on lattice b, and vice versa. There are essentially four different interaction energies, namely ϵ_{AA} for the interaction of an A-atom on lattice a with a neighboring A-atom on lattice b, as well as ϵ_{AB}, ϵ_{BA}, and ϵ_{BB}. Here we may assume that the energy ϵ_{AB} for the interaction energy of an A-atom on lattice a with a B-atom on lattice b is identical with the energy ϵ_{BA}. We now introduce the notations

$$\begin{bmatrix} A & A \\ a & b \end{bmatrix} \quad \begin{bmatrix} A & B \\ a & b \end{bmatrix} \quad \begin{bmatrix} B & A \\ a & b \end{bmatrix} \quad \begin{bmatrix} B & B \\ a & b \end{bmatrix} \tag{18.46}$$

for the numbers of the respective pairs of nearest neighbors.

Here

$$\begin{bmatrix} A & A \\ a & b \end{bmatrix}$$

is the number of nearest neighbor pairs with an A-atom on lattice a and an A-atom on lattice b, etc. If the lattice has the coordination number q, there are, of course, in total again $\frac{1}{2}qN$ pairs. The total energy thus reads as follows:

$$E = \epsilon_{AA}\begin{bmatrix} A & A \\ a & b \end{bmatrix} + \epsilon_{AB}\left(\begin{bmatrix} A & B \\ a & b \end{bmatrix} + \begin{bmatrix} B & A \\ a & b \end{bmatrix}\right) + \epsilon_{BB}\begin{bmatrix} B & B \\ a & b \end{bmatrix} \tag{18.47}$$

We now approximate the numbers in Equation (18.46) quite analogously to Equation (18.35). The probability p_{Aa} of finding an A-atom at a certain position on the lattice a, is

$$p_{Aa} = \frac{2}{N}\begin{bmatrix} A \\ a \end{bmatrix} = x_A(1 + r)$$

since there are exactly $\frac{1}{2}N$ lattice sites available for the $\begin{bmatrix} A \\ a \end{bmatrix}$ A-atoms on lattice a. Analogously, we have for the other probabilities

$$p_{Ab} = \frac{2}{N}\begin{bmatrix} A \\ b \end{bmatrix} = x_A(1 - r)$$

$$p_{Ba} = \frac{2}{N}\begin{bmatrix} B \\ a \end{bmatrix} = (x_B - x_A r)$$

$$p_{Bb} = \frac{2}{N}\begin{bmatrix} B \\ b \end{bmatrix} = (x_B + x_A r)$$

Since there are $\frac{1}{2}qN$ pairs of nearest neighbors, we can make the following approximation for the mean numbers in Equation (18.46) (Bragg–Williams approximation):

$$\begin{bmatrix} A & A \\ a & b \end{bmatrix} = \frac{1}{2}qNp_{Aa}p_{Ab} = \frac{1}{2}qNx_A^2(1 - r^2)$$

$$\begin{bmatrix} A & B \\ a & b \end{bmatrix} = \frac{1}{2} qNp_{Aa}p_{Bb} = \frac{1}{2} qNx_A(1+r)(x_B + x_A r)$$

$$\begin{bmatrix} B & A \\ a & b \end{bmatrix} = \frac{1}{2} qNp_{Ba}p_{Ab} = \frac{1}{2} qNx_A(1-r)(x_B - x_A r)$$

$$\begin{bmatrix} B & B \\ a & b \end{bmatrix} = \frac{1}{2} qNp_{Ba}p_{Bb} = \frac{1}{2} qN(x_B - x_A r)(x_B + x_A r) \qquad \textbf{(18.48)}$$

One convinces oneself that the sum of the numbers in Equation (18.48) is exactly $\frac{1}{2}qN(p_{Aa} + p_{Ba})(p_{Ab} + p_{Bb}) = \frac{1}{2}qN$; i.e., the total number of all neighbor pairs. If one inserts Equation (18.48) into (18.47), it follows for the dependence of the total energy on the order parameter r that

$$E = \frac{1}{2} qN \left\{ \epsilon_{AA} x_A^2 + 2\epsilon_{AB} x_A x_B + \epsilon_{BB} x_B^2 \right\} - qNx_A^2 \epsilon r^2$$

where $\epsilon = \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) - \epsilon_{AB}$. This expression corresponds to Equation (18.38).

We are now also able to calculate the entropy of the system, or the number of states for given r:

$$S = k \ln \left\{ \frac{\left(\frac{N}{2}\right)!}{\begin{bmatrix} A \\ a \end{bmatrix}! \begin{bmatrix} B \\ a \end{bmatrix}!} \frac{\left(\frac{N}{2}\right)!}{\begin{bmatrix} A \\ b \end{bmatrix}! \begin{bmatrix} B \\ b \end{bmatrix}!} \right\}$$

This expression corresponds also to Equation (18.34) but now the two sublattices must be treated separately. If one inserts here the expressions (18.45) and exploits Stirling's approximation, one obtains

$$S = -\frac{1}{2} Nk \left[x_A(1+r) \ln\{x_A(1+r)\} + (x_B - x_A r) \ln\{x_B - x_A r\} \right.$$
$$\left. + x_A(1-r) \ln\{x_A(1-r)\} + (x_B + x_A r) \ln\{x_B + x_A r\} \right]$$

We are now looking for the minimum of the free energy with respect to the order parameter r, since this is the most probable state of the system (equilibrium state):

$$\frac{\partial F}{\partial r} = \frac{\partial}{\partial r}(E - TS) = 0$$

This requires that

$$\frac{qx_A\epsilon}{kT} r = \frac{1}{4} \ln \left(\frac{1+r}{1-r} \frac{x_B + x_A r}{x_B - x_A r} \right)$$
$$= \frac{1}{4} \ln \left(\frac{1+y}{1-y} \right) \qquad \text{with} \quad y = \frac{r}{x_B + x_A r^2}. \qquad \textbf{(18.49)}$$

The last equality follows, since $x_A + x_B = 1$. If one employs the definition of the arctanh function,

$$\operatorname{arctanh} x = \frac{1}{2} \ln \left(\frac{1+x}{1-x} \right)$$

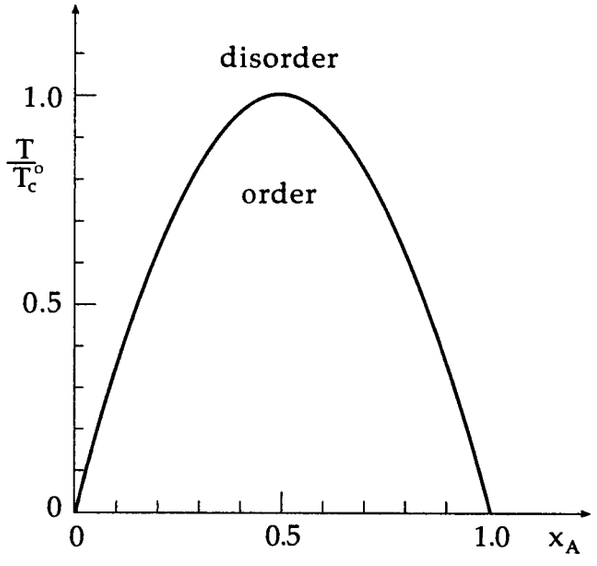


Figure 18.10. Dependence of the critical temperature on the concentration of the A-atoms.

one can write Equation (18.49) in more convenient form:

$$\frac{r}{x_B + x_A r^2} = \tanh\left(\frac{2qx_A\epsilon}{kT}r\right)$$

Again we get a self-consistent equation to determine the order parameter r. It has to vanish in the vicinity of the phase transition ($r \to 0$), so that we may expand $\tanh x$ for small arguments in the well-known way, while on the left-hand side the quadratic term in the denominator can be neglected,

$$\frac{r}{x_B} \approx \frac{2qx_A\epsilon}{kT}r$$

The critical temperature T_c depends on the concentration of the atoms (Figure (18.10),

$$kT_c = 2q\epsilon x_A x_B = 2q\epsilon x_A(1 - x_A)$$

One obtains a parabolic dependence of the critical temperature on the concentration. The highest critical temperature T_c is achieved for equal concentrations $x_A = x_B = \frac{1}{2}$. It has the value $T_c^0 = \frac{1}{2}q\epsilon/k$.

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